Annex A

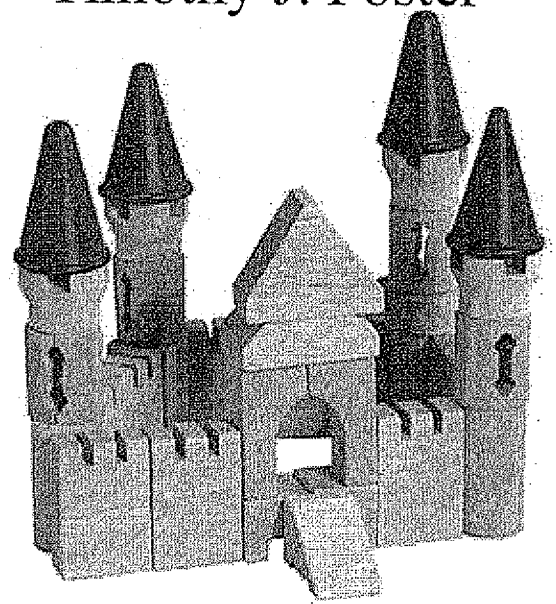
STEP ITN

MARIE CURIE ACTIONS

Hydrocolloids Structure and Properties

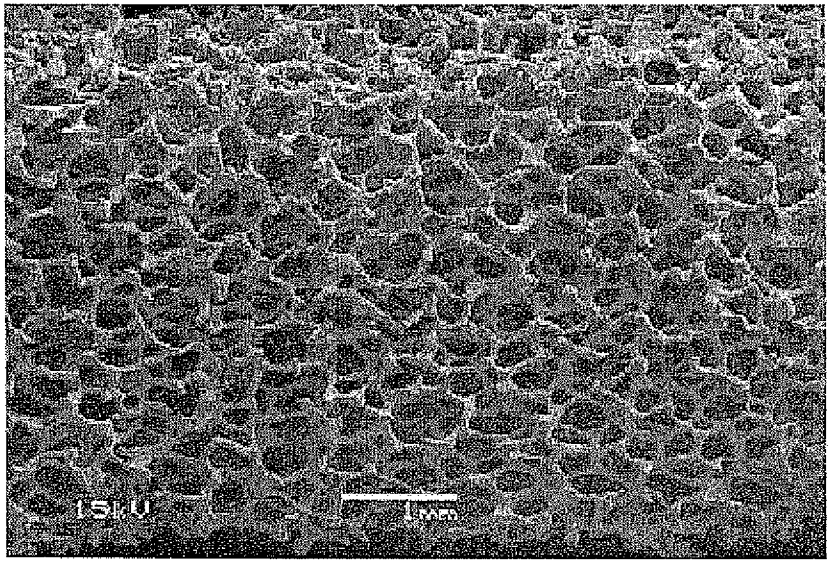
The building blocks for structure

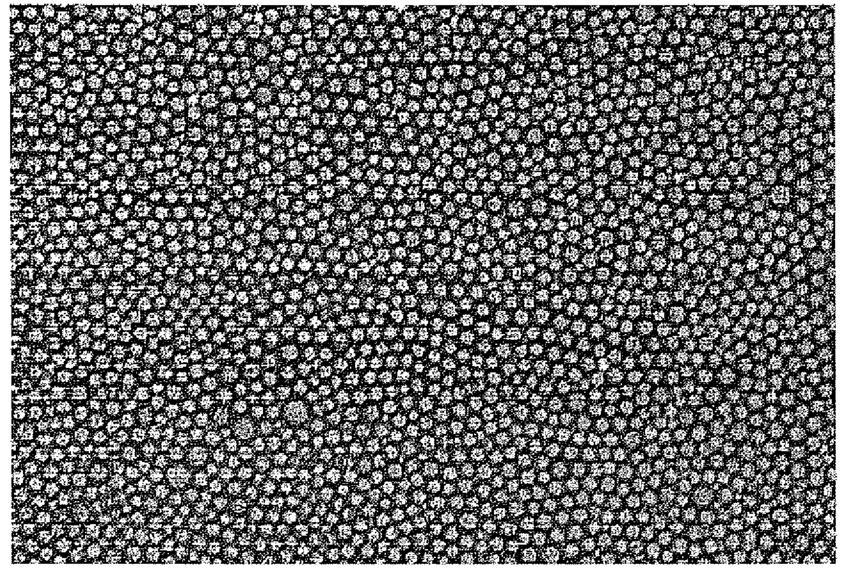
Timothy J. Foster



18 month Meeting, Unilever Vlaardingen, March 29-31, 2010

The University of Nottingham

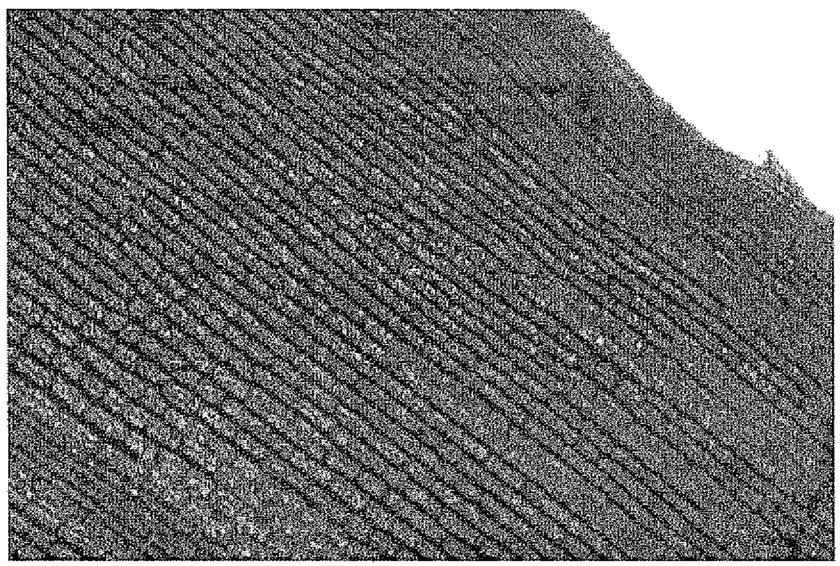




Manufactured Materials

Foams

Emulsions

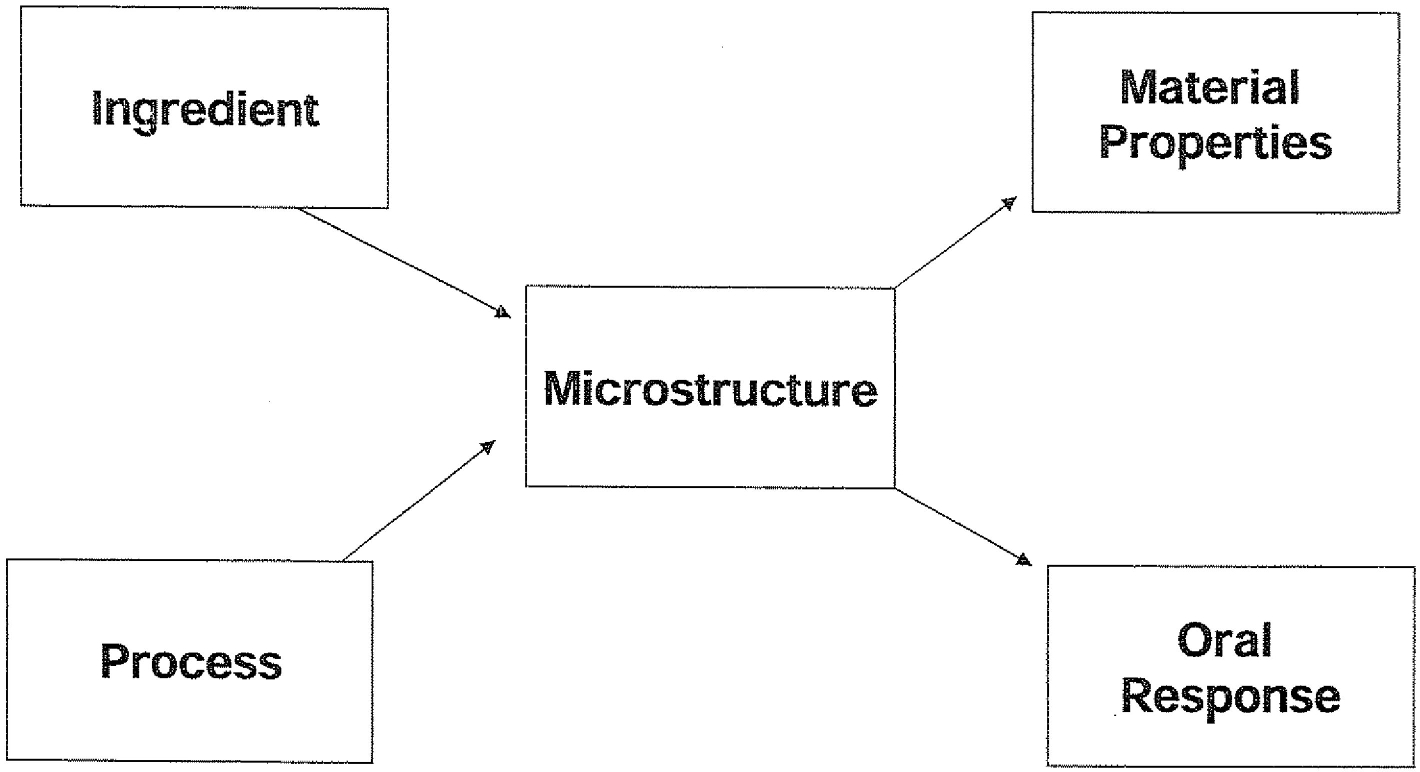


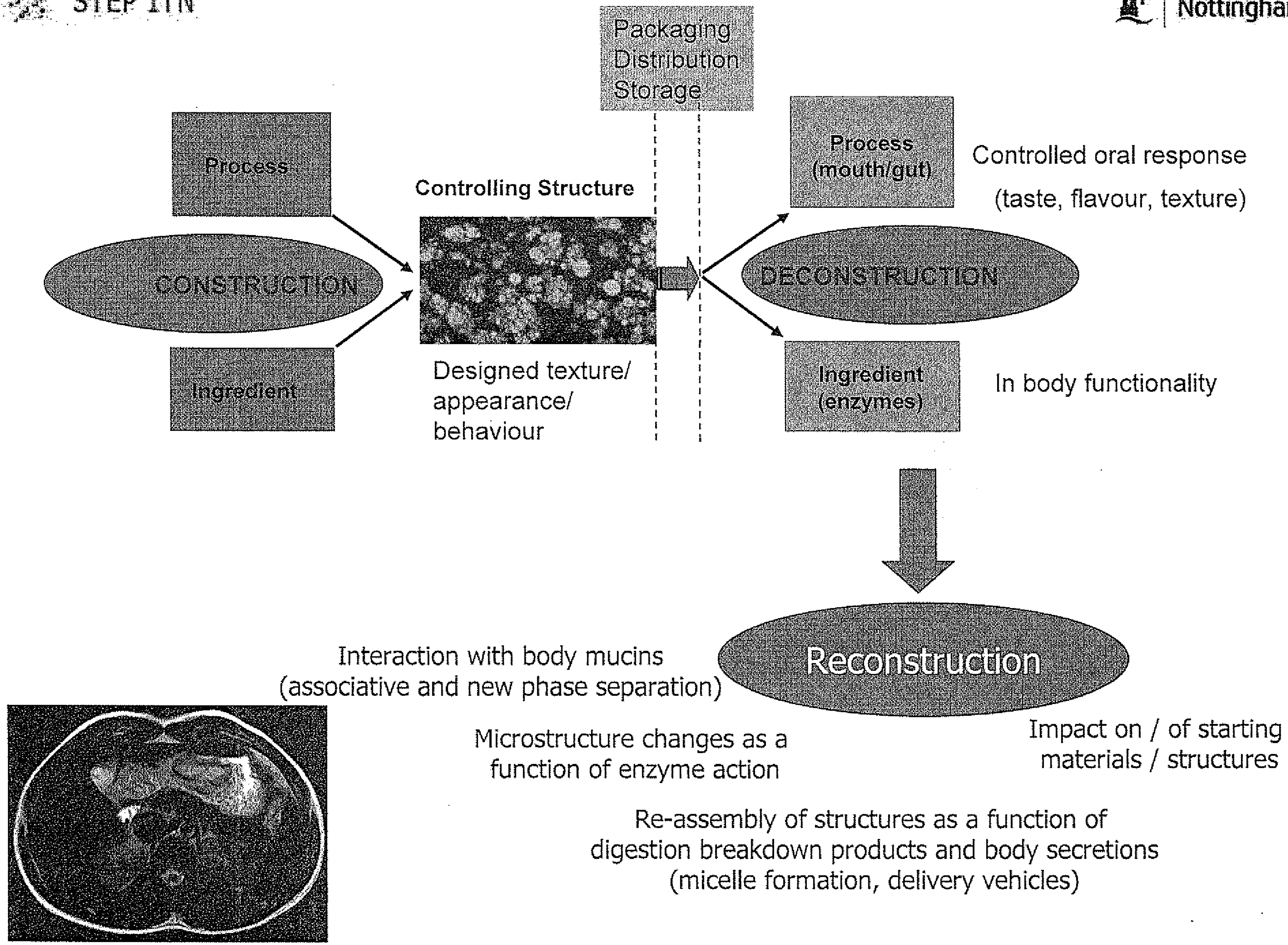
Natural Materials

This shows a layer of onion (Allium) cells.

Targeting Hydrocolloids For Specific Applications:

Approach




Packaging
Distribution
Storage
Process
CONSTRUCTION
Ingredient
Controlling Structure
Designed texture/
appearance/
behaviour
Process
(mouth/gut)
DECONSTRUCTION
Ingredient
(enzymes)
Controlled oral response
(taste, flavour, texture)
In body functionality
Reconstruction
Interaction with body mucins
(associative and new phase separation)
Microstructure changes as a
function of enzyme action
Impact on / of starting
materials / structures
Re-assembly of structures as a function of
digestion breakdown products and body secretions
(micelle formation, delivery vehicles)

Single Biopolymer systems

Hydrocolloid Structure/ Function

Need:

- define biopolymer primary structure
- understand the nature of the interaction / rates
- understand the solvent effects
- measure material properties
- test influence of primary structure variation and changes in environmental conditions on mechanical properties.

Hydrocolloid Materials & Function

- Gelling
  - Pectin
  - Alginate
  - Starch
  - Agar
  - Carrageenan
  - Gellan
  - Gelatin
  - Milk proteins
  - Egg proteins
- Thickening
  - Pectin
  - Alginate
  - Starch
  - LBG
  - Guar gum
  - Xanthan
- Emulsification
  - Gelatin
  - Milk proteins
  - Egg proteins
  - Soya proteins
  - Pea proteins
  - Gum Arabic

Hydrocolloid Materials & Function

Gelling
- Pectin
- Alginate
- Starch
- Agar
- Carrageenan
- Gellan
- Curdlan
- Celluosics
- Succinoglycan
- Scleroglucan
- Mixtures

Thickening
- Pectin
- Alginate
- Starch
- LBG
- Guar Gum
- Xanthan
- lamda Carrageenan
- Cellulosics
- Beta Glucan

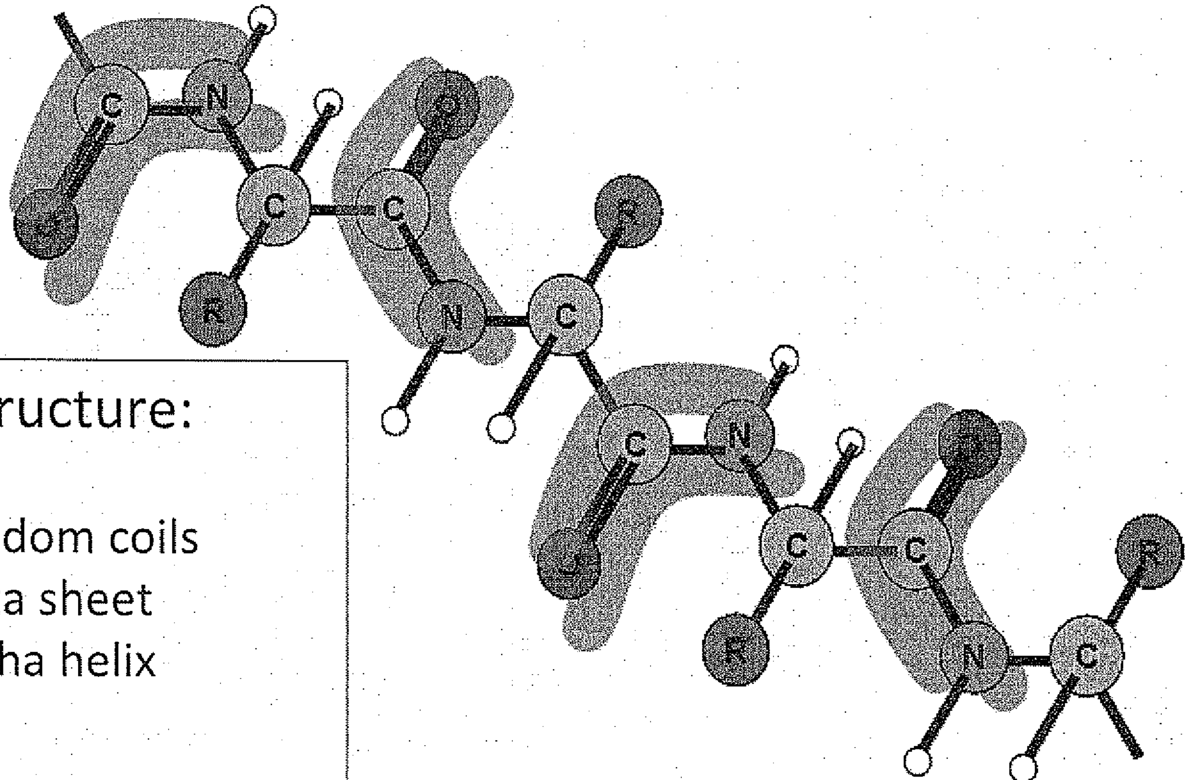
Emulsification
- Gum Arabic
- Propylene glycol Alginate
- Sugarbeet pectin
- OSA starch

Protein structure

A protein is a <u>polymer</u> of <u>amino acids</u>

- Primary structure
  - amino acid sequence
- Secondary structure
  - spatial structure through interactions between amino acids that are *near* along the amino acid chain (e.g. α-helix, β-sheet)
- Tertiary structure
  - spatial structure through interactions between amino acids that are *far away* along the amino acid chain
- Quaternary structure
  - association of different amino acid sequences (e.g. haemoglobin)

Protein



Protein Structure:

Backbone

- random coils
- beta sheet
- alpha helix

Charge

Determines Properties:

Interfacial properties

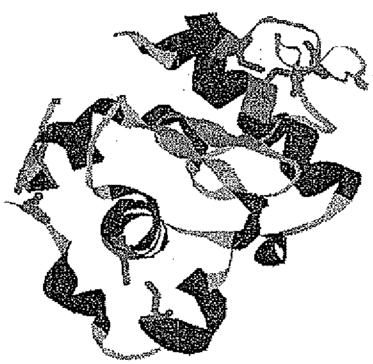
- foams
- emulsions

Gel forming

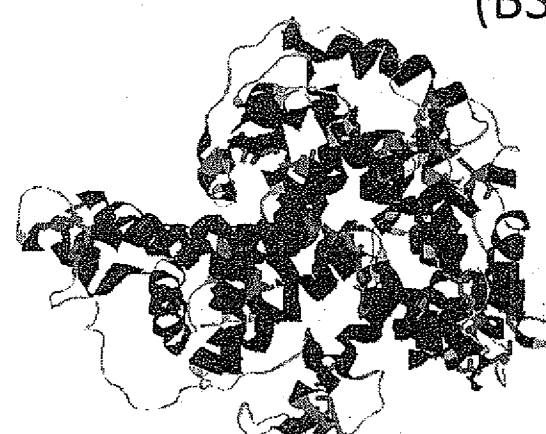
Structure of globular proteins

β-lactoglobulin (β-lg)
dimeric form at neutral pH

α-lactalbumin (α-la)



bovine serum albumin (BSA)



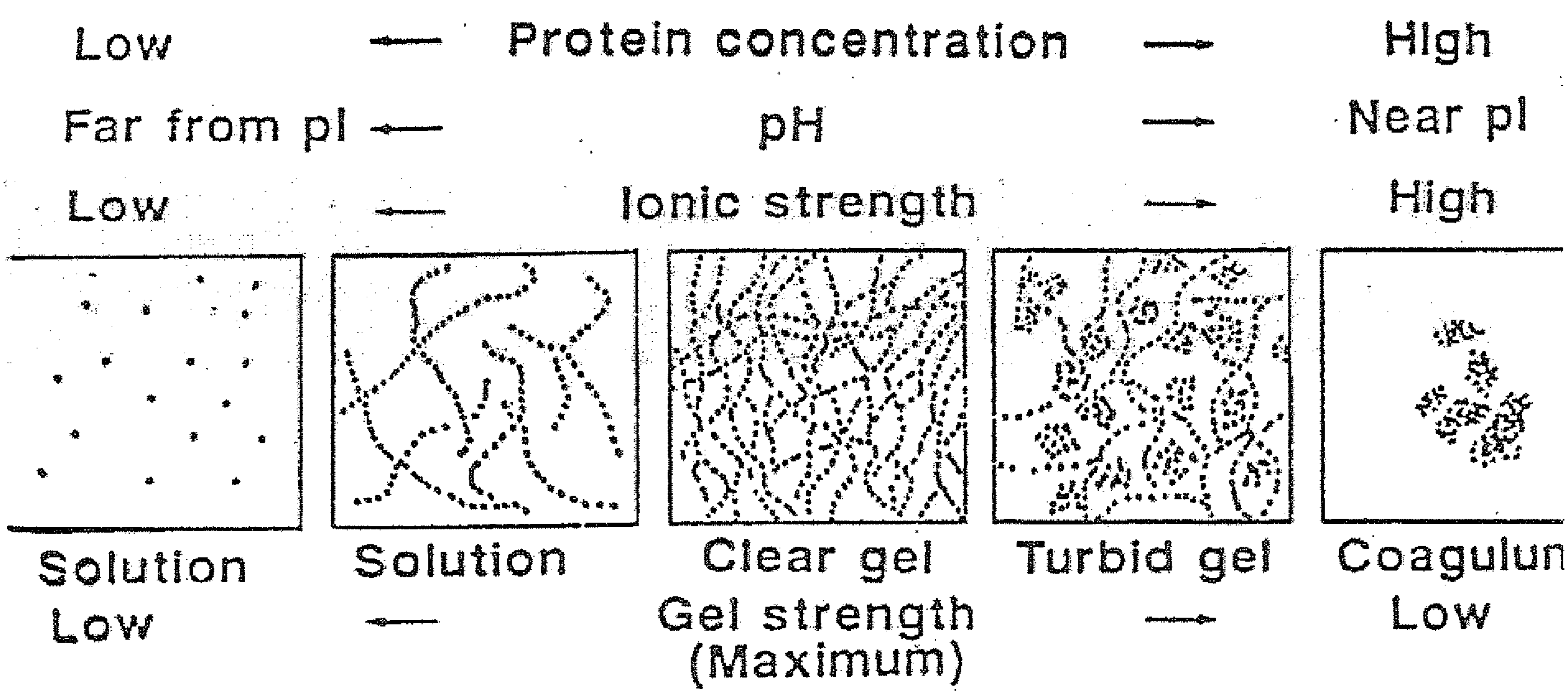
Color caption:

α-Helix

β-Sheets

Cysteines

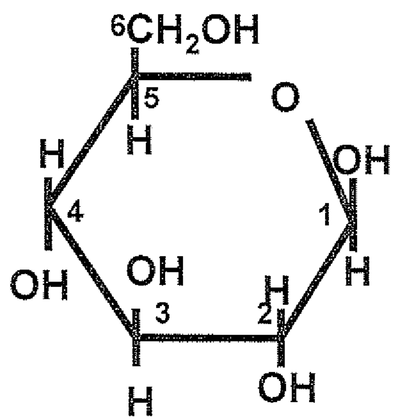
Turbid Gels



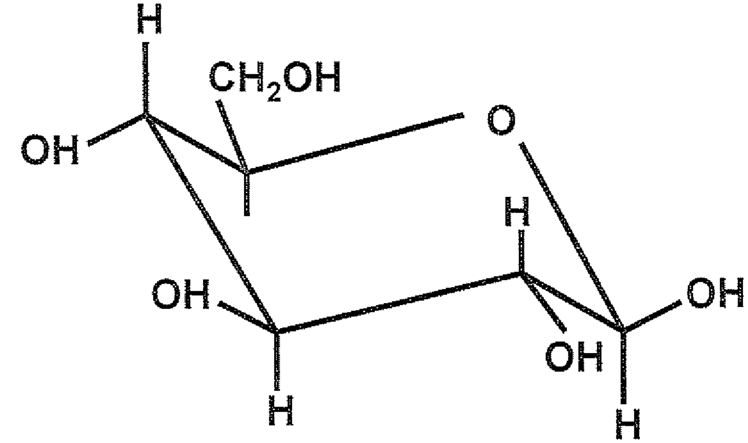
Low ← Protein concentration → High
Far from pI ← pH → Near pI
Low ← Ionic strength → High
Solution
Solution
Clear gel
Turbid gel
Coagulun
Low ← Gel strength (Maximum) → Low

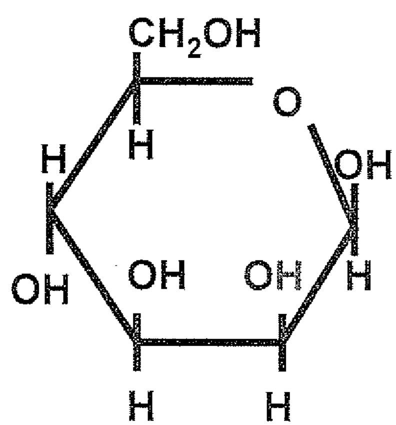
Carbohydrates…what do they look like?

- How do they differ?



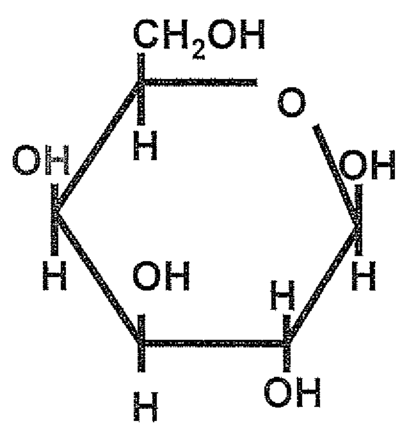
Glucose

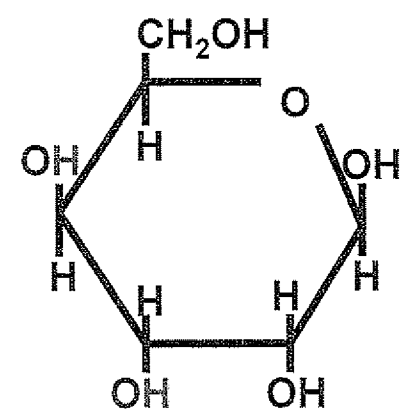




Mannose

Galactose

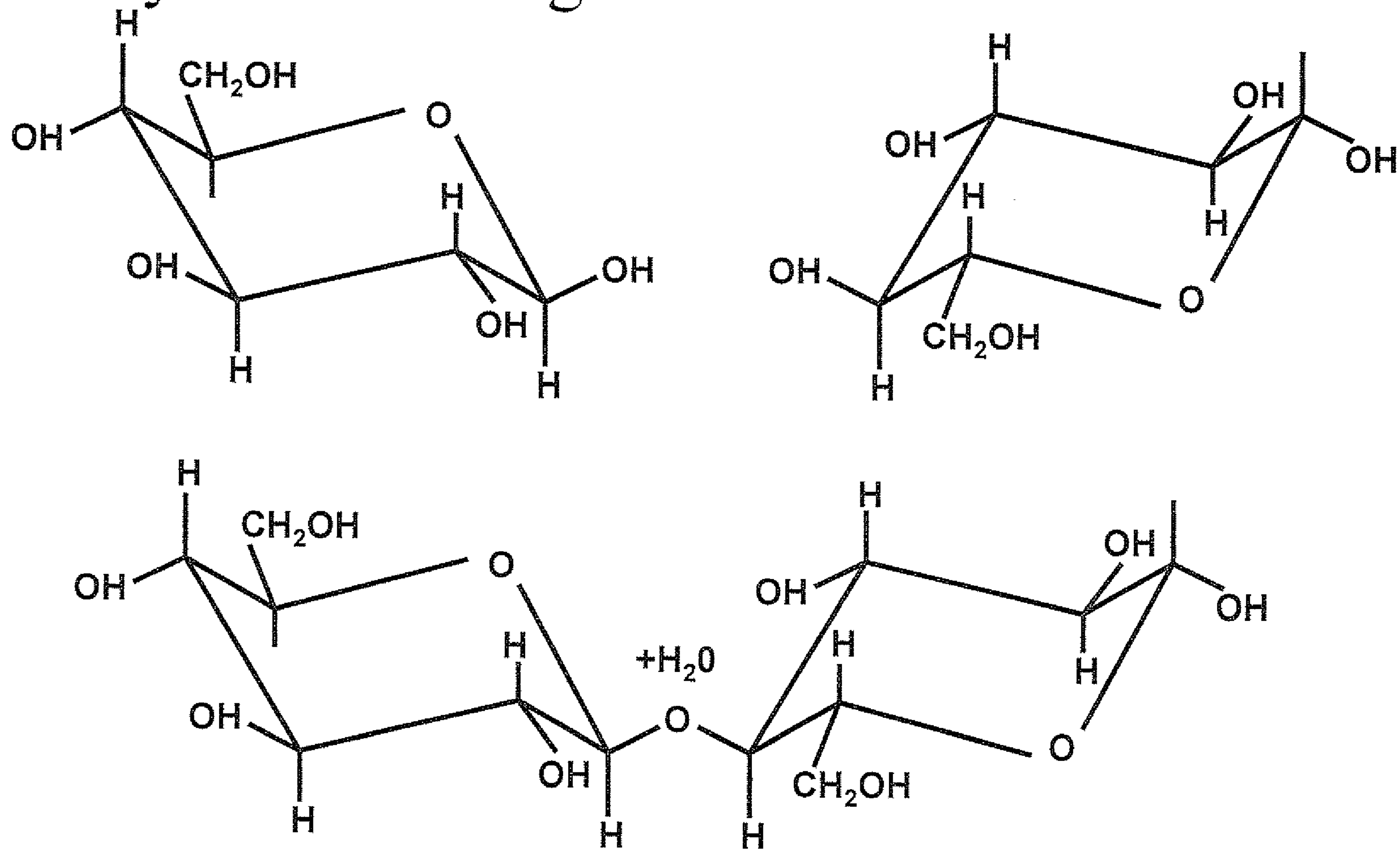


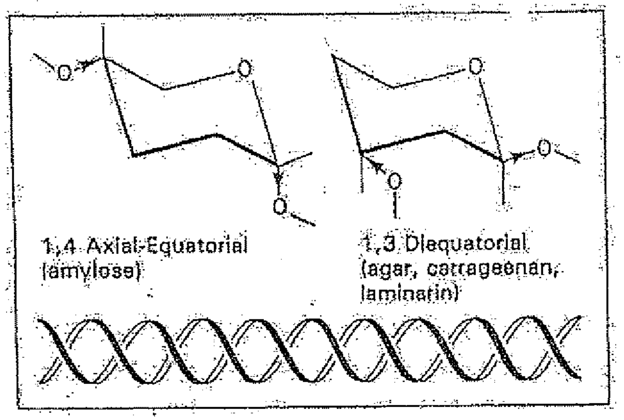


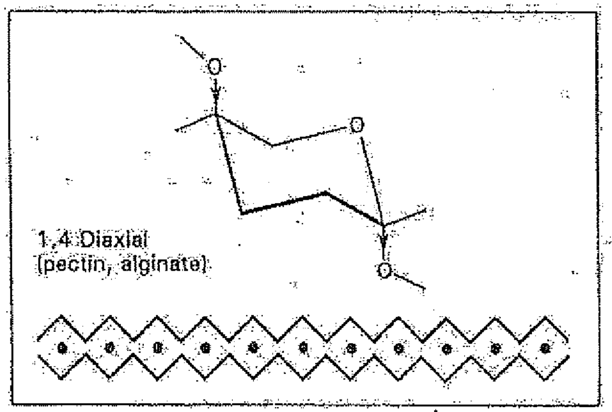
Gulose

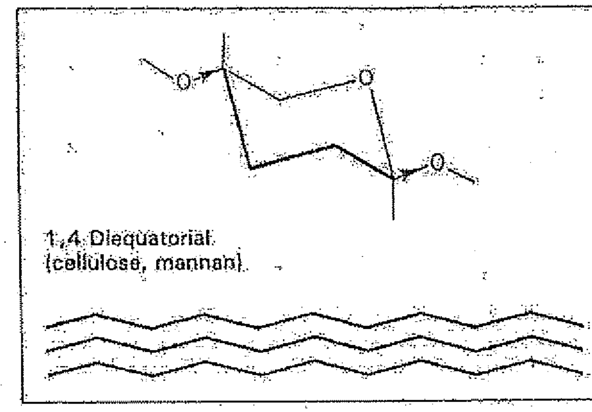
Sugar Interactions

- Glycosidic linkage



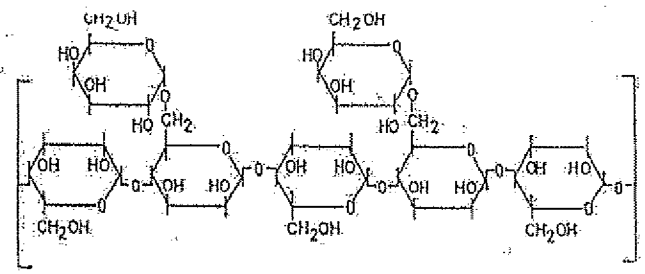


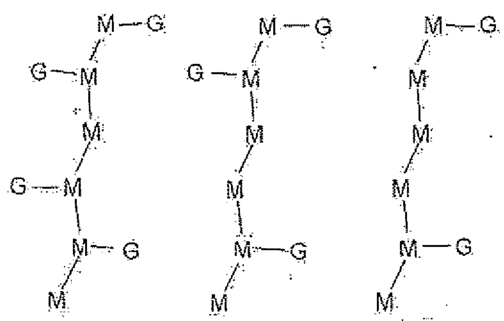




LBG is a *galactomannan.*

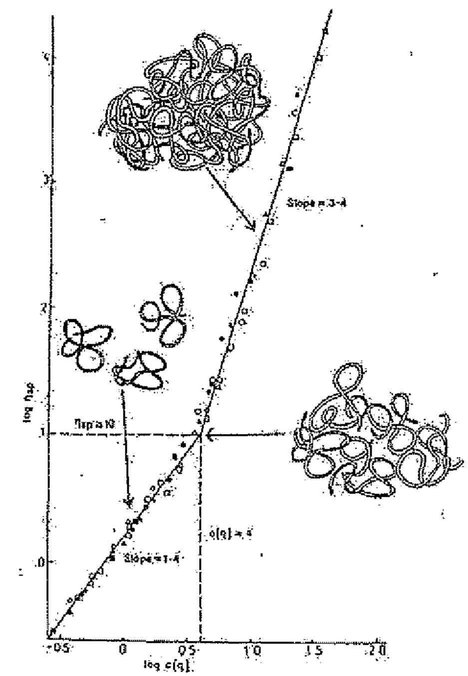
(1-4) β-D-mannose





Polysaccharide Structure / Functionality

Taking into account the volume swept out by each biopolymer chain (c[η]), the point of coil overlap/ entanglement (c*) can be obtained.



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Sources of hydrocolloids

Botanical

starch, cellulose, galactomannans, pectin, gum arabic, karaya, tragacanth, beta glucan

Seaweeds

agar, carrageenan, alginate

Animal

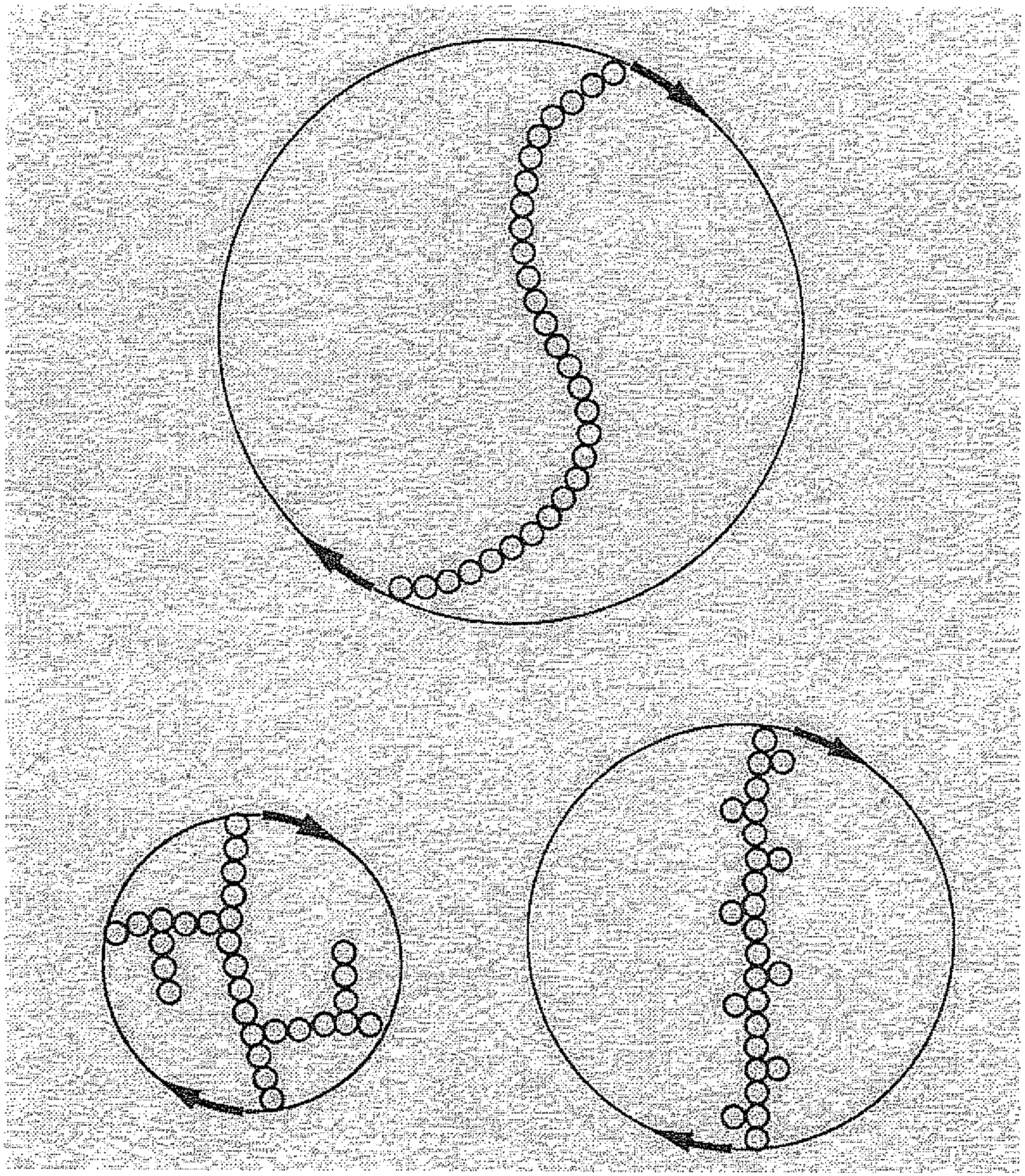
gelatin, chitosan, hyaluronan

Bacterial

xanthan, gellan, dextran

Structural Features

- Linear
  - (homo- and hetero-)
- Linear – branched
  - (homo- and hetero-)
- Branched
  - (homo- and hetero-)
- Ordered helices
  - (single, double, triple)



Polysaccharide thickeners

- The most efficient thickeners are;

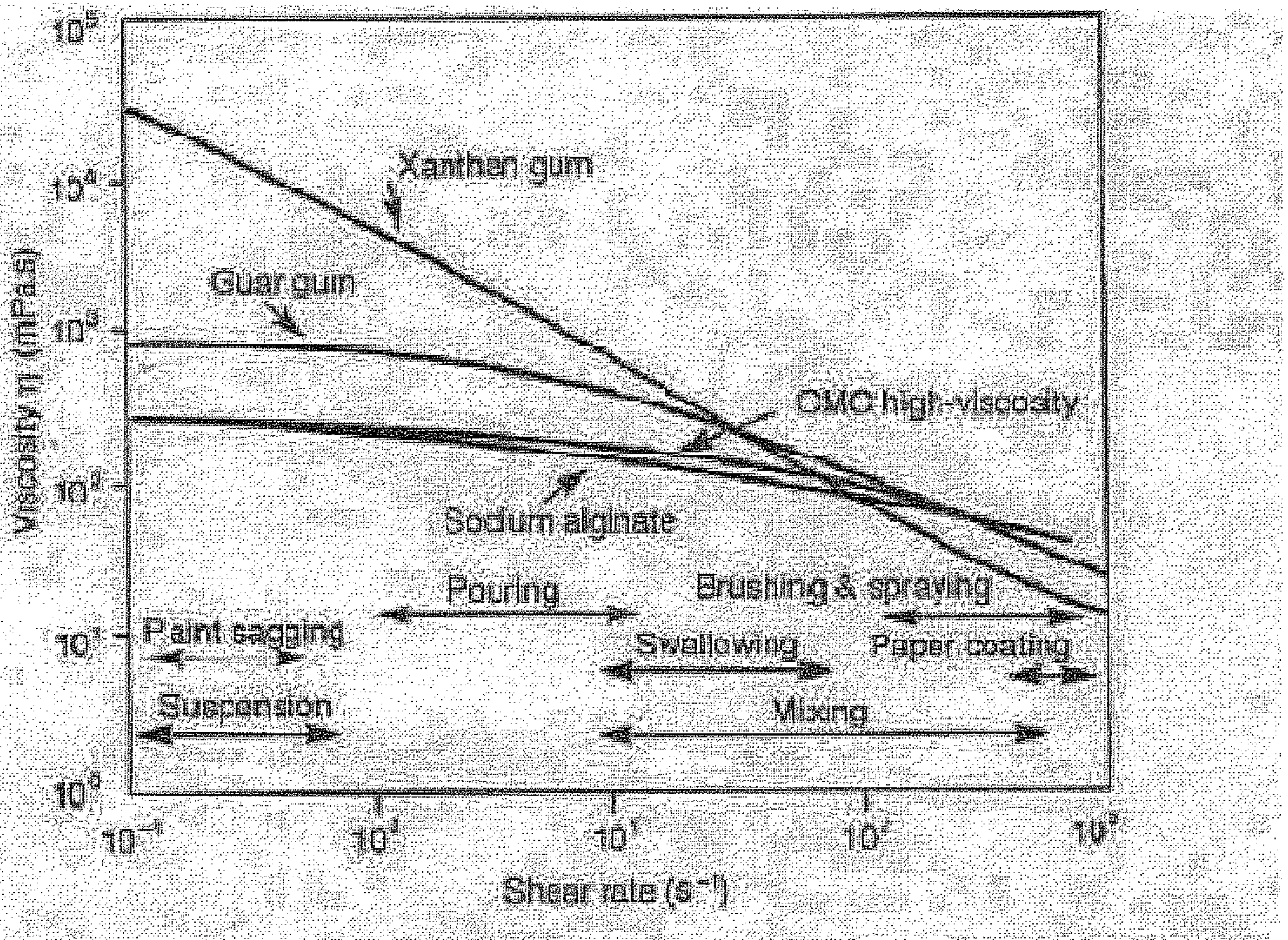
- Linear,
- High molecular mass
- Charged

Alternative Hydrocolloids

Cashew Gum
Gum Karaya
Okra Gum
Caramania Gum (almond)
Cassava Starch
Chia Gum
Cocoyam Flour
Cowpea protein /starch
Detarium microcarpum polysaccharide
Flaxseed Gum
Hsian-tsao Leaf gum (Taiwan/China)
Lichenin
Lupin Protein
Moussul Gum (Plum)
Portulaca Oleracea
Psyllium gum
Rice Flour
Sassa Gum
Soy Bean Polysaccharide
Tara Gum
Tropical Starches
Yellow Mustard Gum

Aloe Gum
Gum Ghatti
Oat gum
Gum Tragacanth
Cassia Gum
Cherry Gum
Chickpea Flour
Combretum Gum
Cyclodextrins
Fenugreek gum
Gleditsia macracantha
Lesquerella Gum
Lucaena galactomannan
Manna Gum
Opuntia Ficus
Prickly Pear
Quince seed gum
Rye bran (beta d glucan / arabinoxylan)
Sorghum flour
Tamarind gum
Tremella Aurantia Poysaccharide
Yam

Typical Solution Properties



Comparison of the flow behaviour of xanthan gum to other hydrocolloid solutions (0.5% concentration).

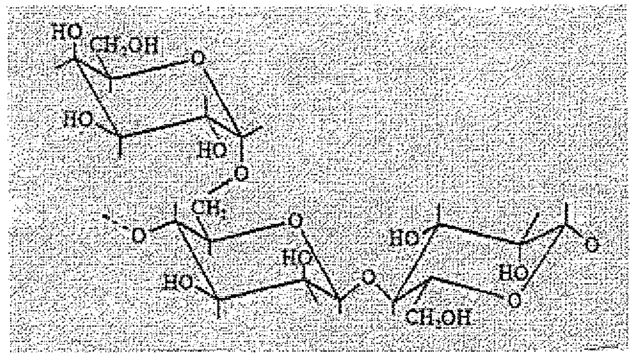
Hydrocolloid Structure/ Function

Need:

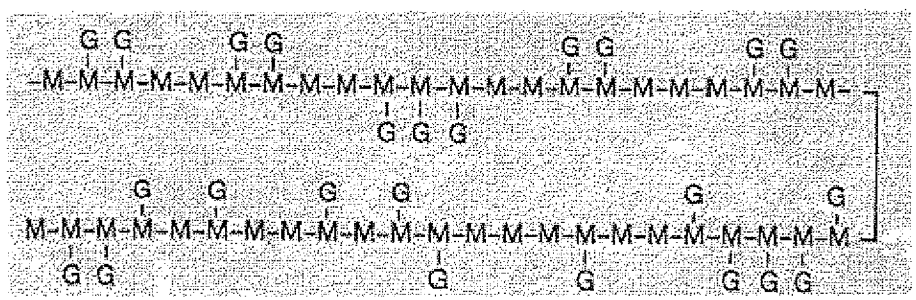
- define biopolymer primary structure
- understand the nature of the interaction / rates
- understand the solvent effects
- measure material properties
- test influence of primary structure variation and changes in environmental conditions on mechanical properties.

Galactomannans

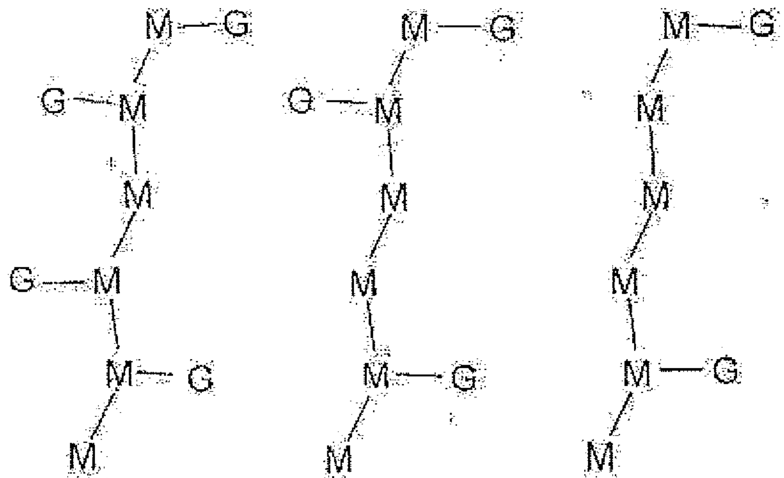
- Galactomannans include guar gum, locust bean gum (carob), fenugreek, cassia and tara gum.
- They have a high molecular mass (~ in excess of 500kDa) and consist of β 1,4 linked mannose residues with galactose units linked α 1,6.



- The M:G ratio is ~2:1 for guar, 3:1 for tara and 4:1 for locust bean gum.
- The galactose units are not evenly distributed along the chain.



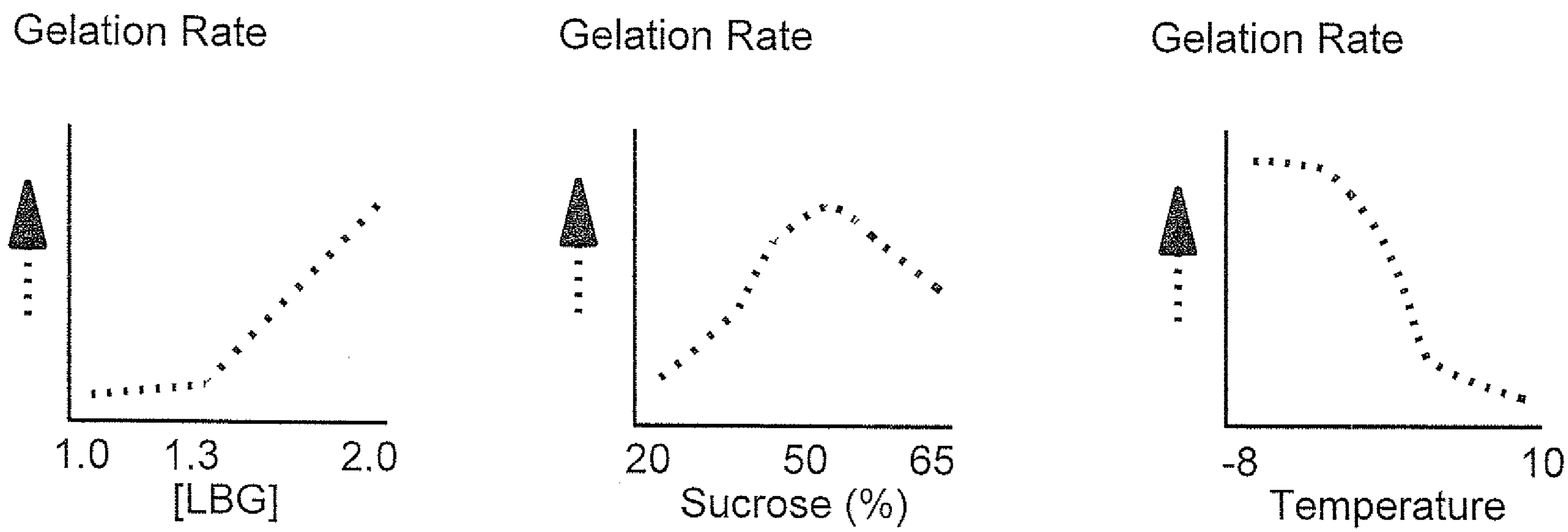
LBG Structure / Functionality



Guar 40% G | QSG's 40-10% G | LBG 23% G

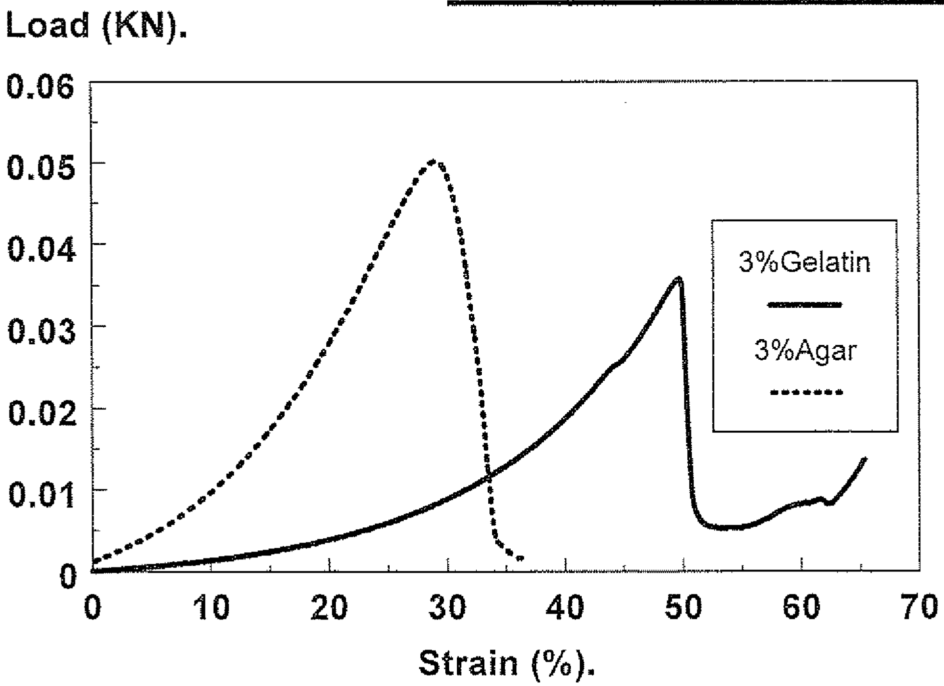
- LBG can be fractionated wrt temperature of solubility.
- Cold soluble LBG (30C) has a higher G/ M than that soluble at high temperature (80C).
- LBG soluble at 80C has a galactose content of 16.6%, and gels at ambient temperature.
- Cold soluble LBG does NOT gel even when frozen & thawed.
- Not necessary for ice to be present, a non-ionic interaction, dependent on solvent quality.

- The distribution of galactose sidechains is all important in dictating functionality.



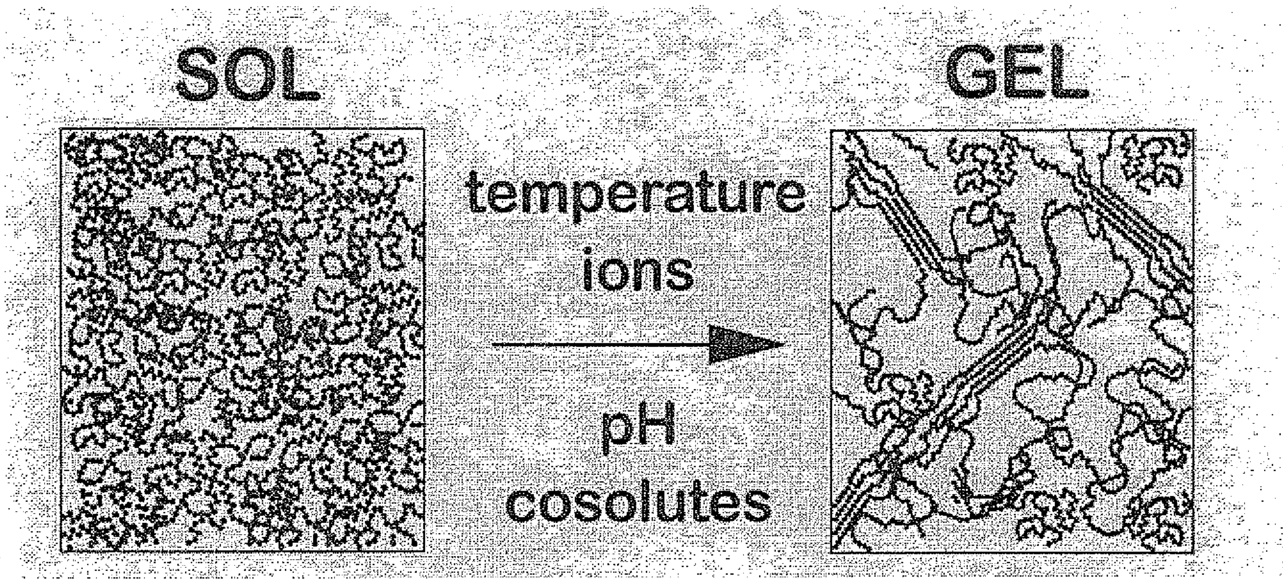
- Self association is kinetically controlled as a function of the number of available junction zones

Properties of Hydrocolloids



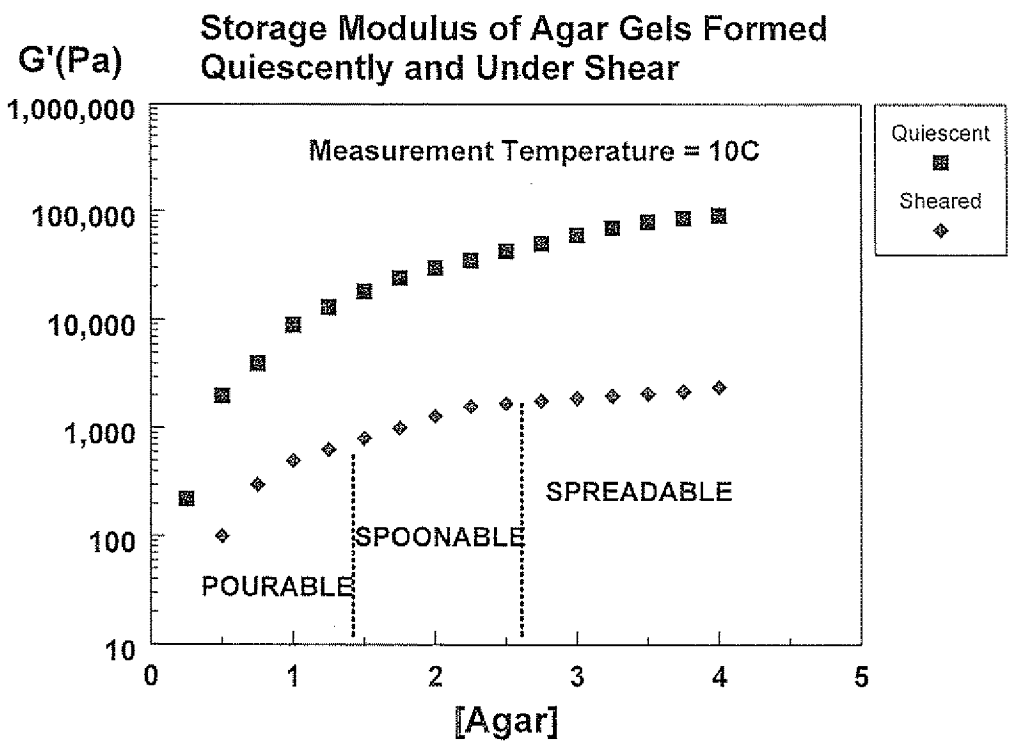
Typical polymer gel properties

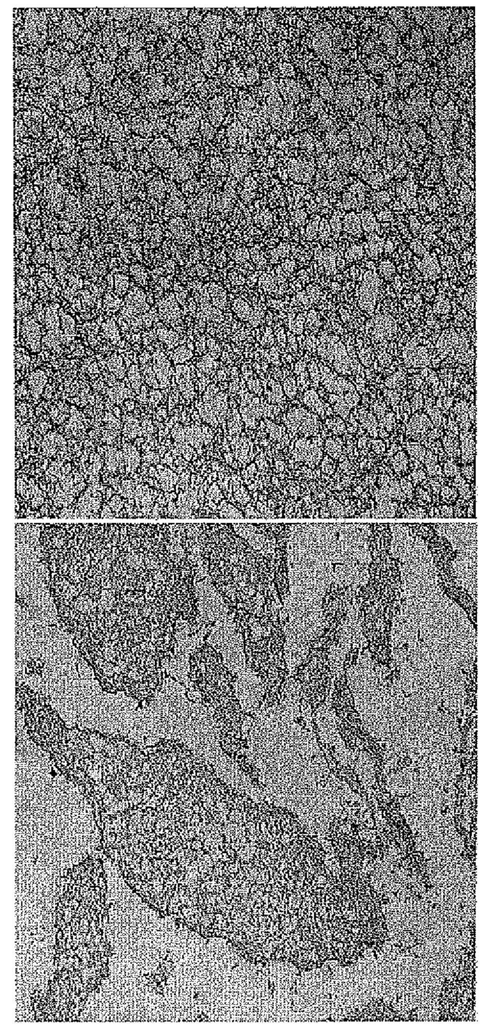
Dependent on Solvent quality, Polymer fine structure, Junction zone type / quantity



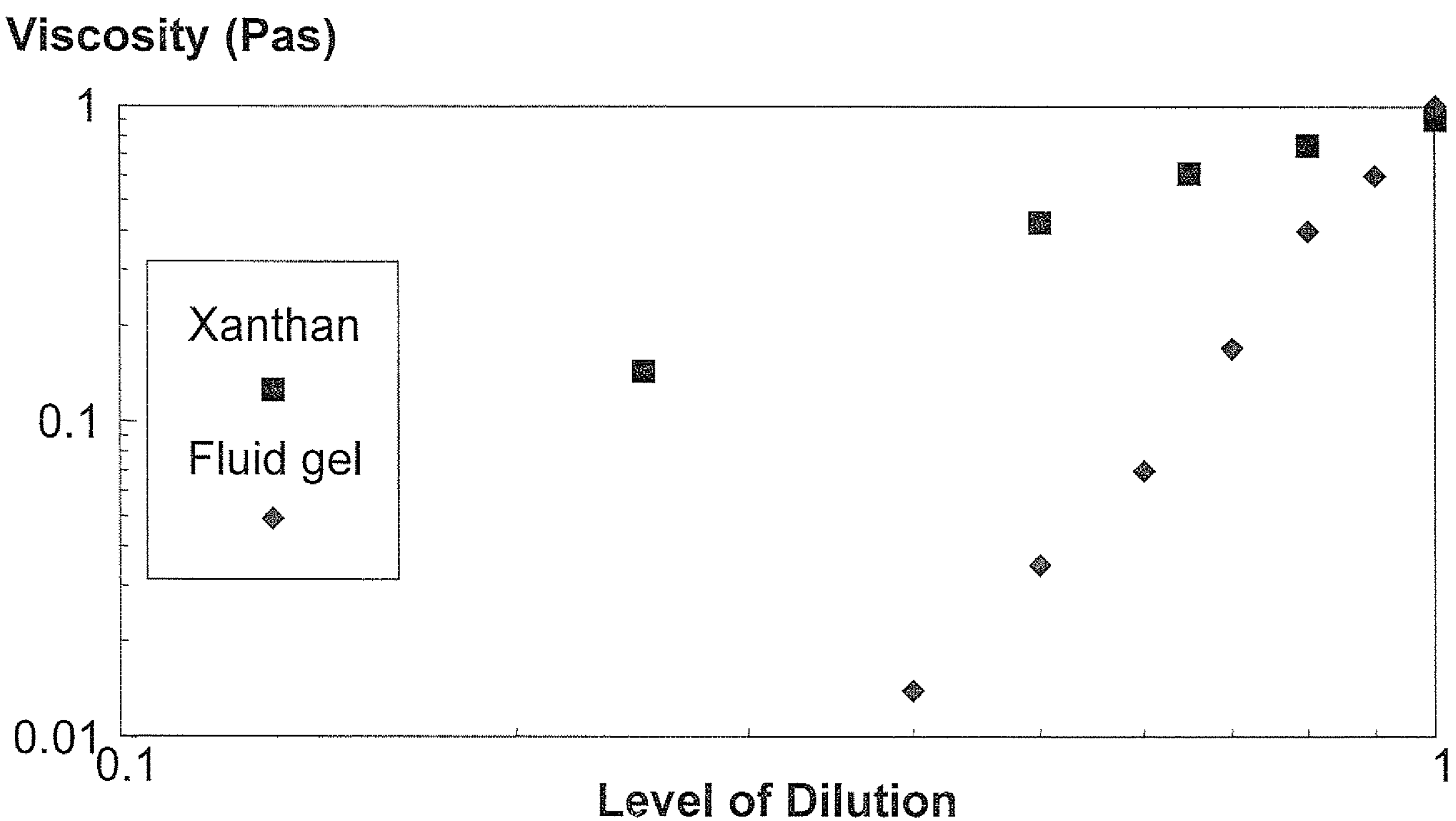
Effect of Shear during Gelation: Fluid gel Particle formation

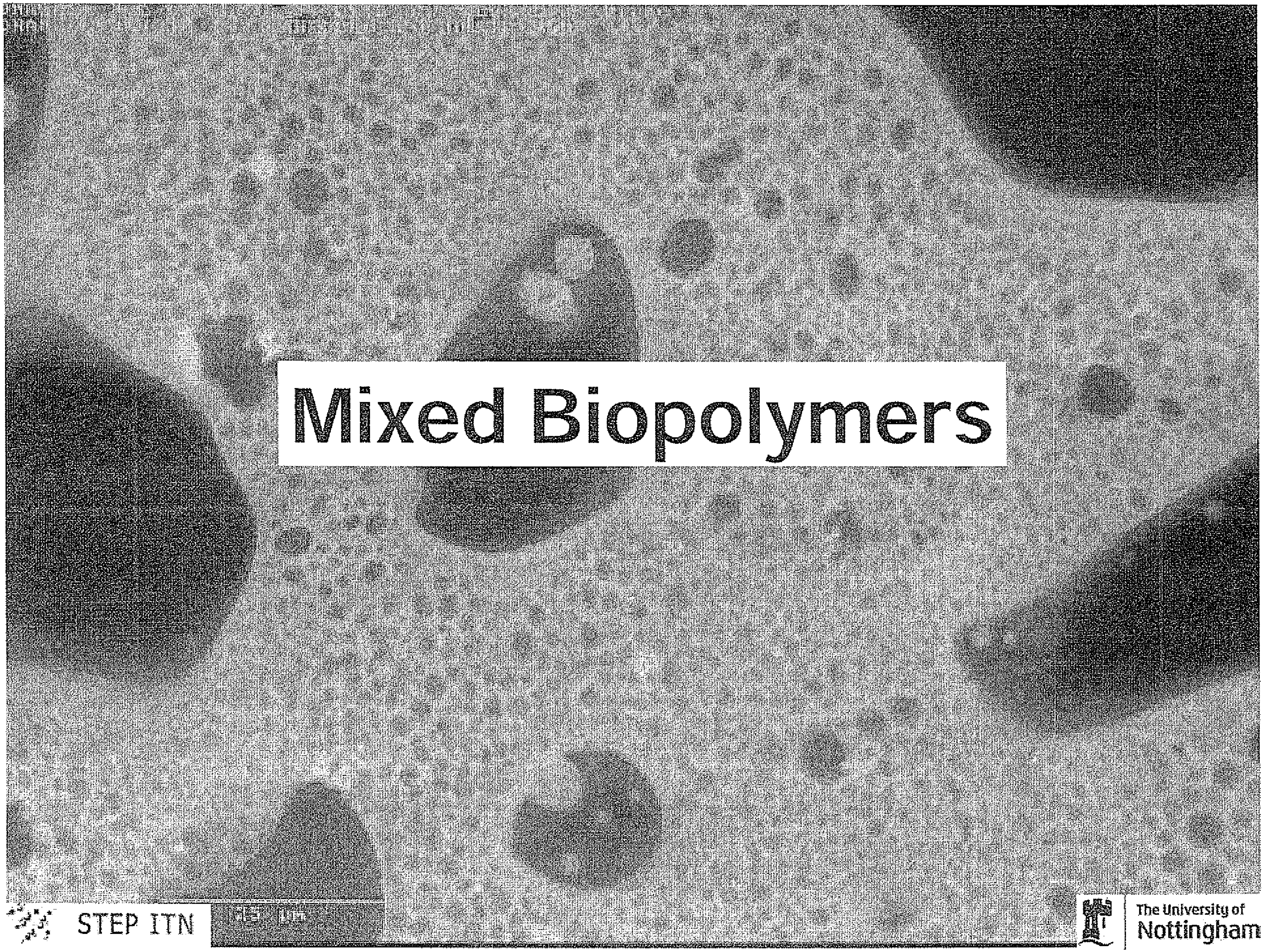
- Composite properties are dependent upon the number and size of particles produced.
  - This in turn is dependent upon the polymer used, the polymer concentration and the shear field.



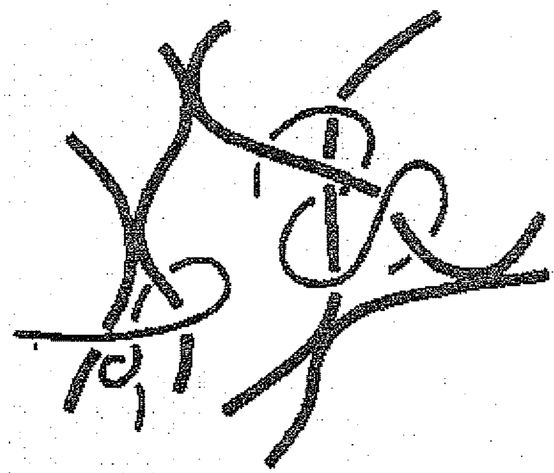


- Due to the colloidal nature of their properties they provide better dilution characteristics than their molecular counterparts.

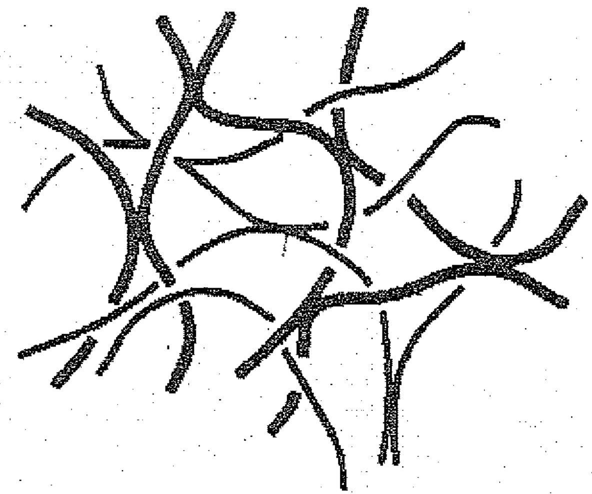




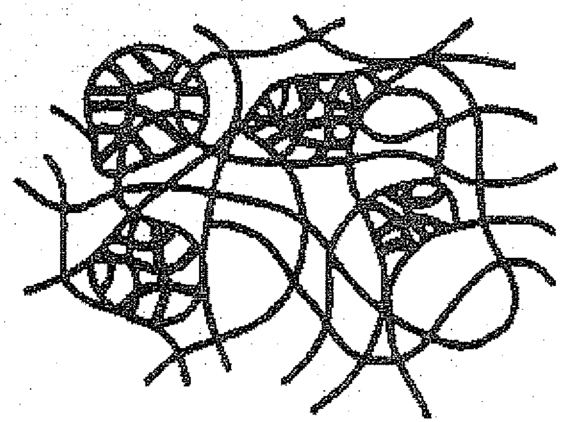
Mixed Biopolymers



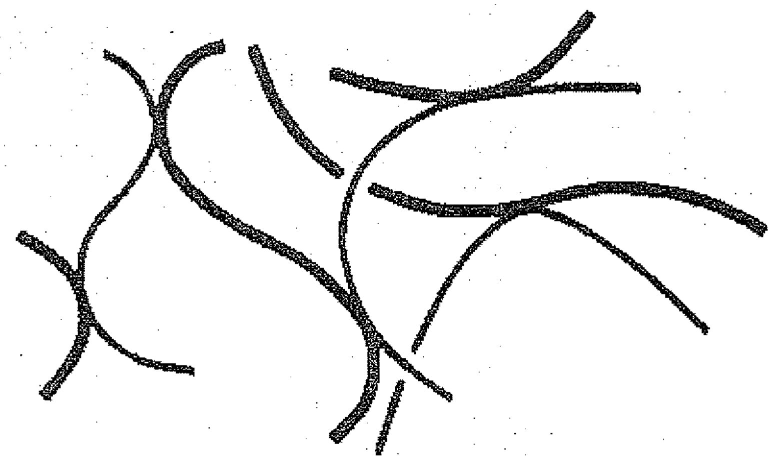
Swollen network



Interpenetrating network



Phase separated network

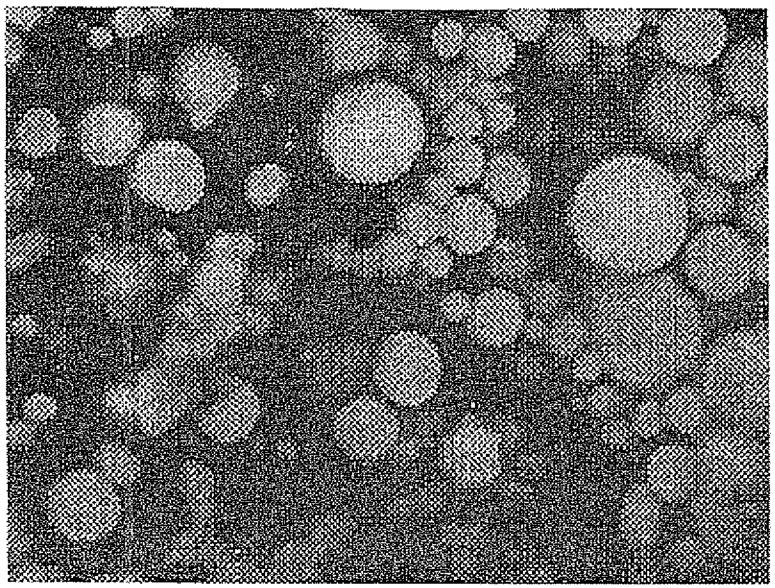


Coupled network

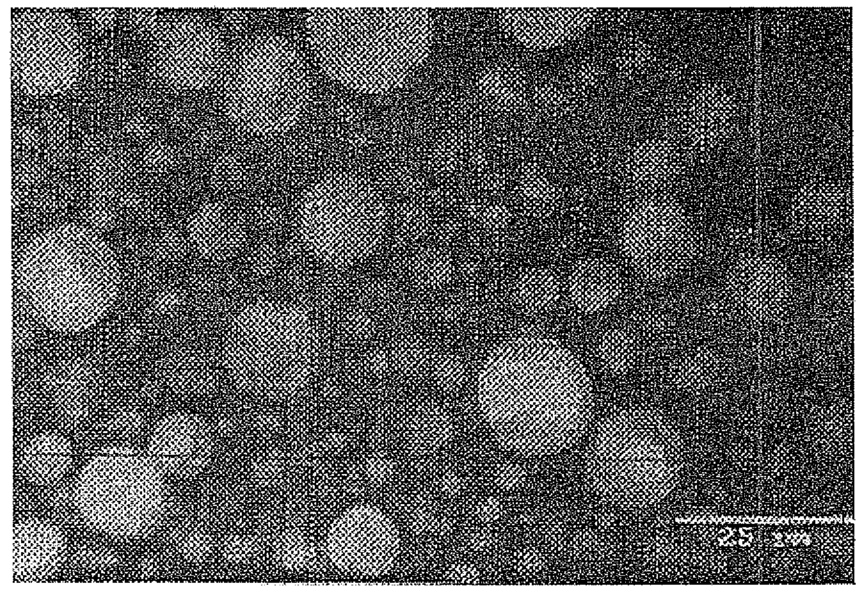
Aqueous-based two-phase systems

Microstructure

o/w emulsion

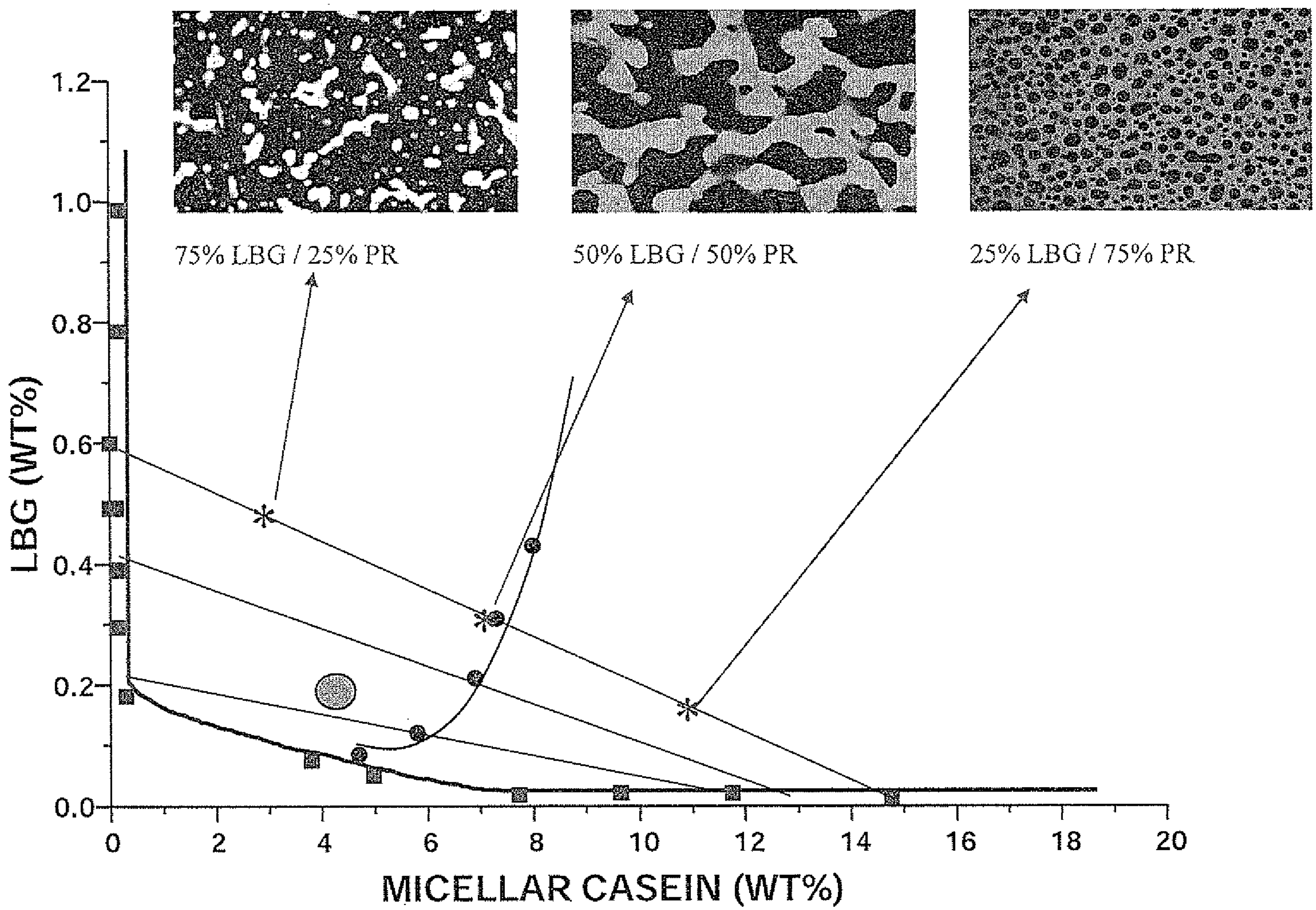


water-in-water emulsion



25 μm

Phase Separation phenomena is used in the creation of food products.

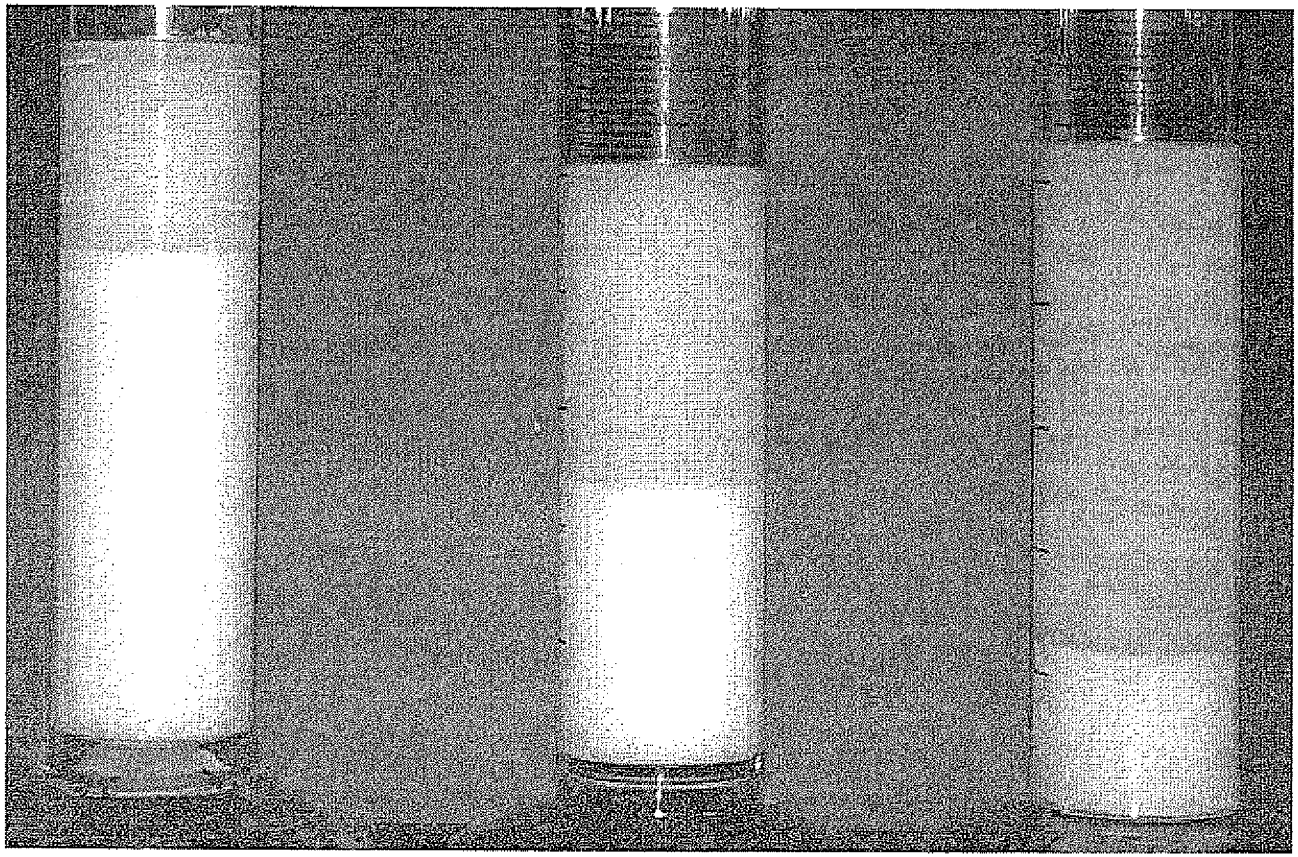


Phase diagram measured at 5C

Top phase: Gelatin

Aqueous-based two-phase systems

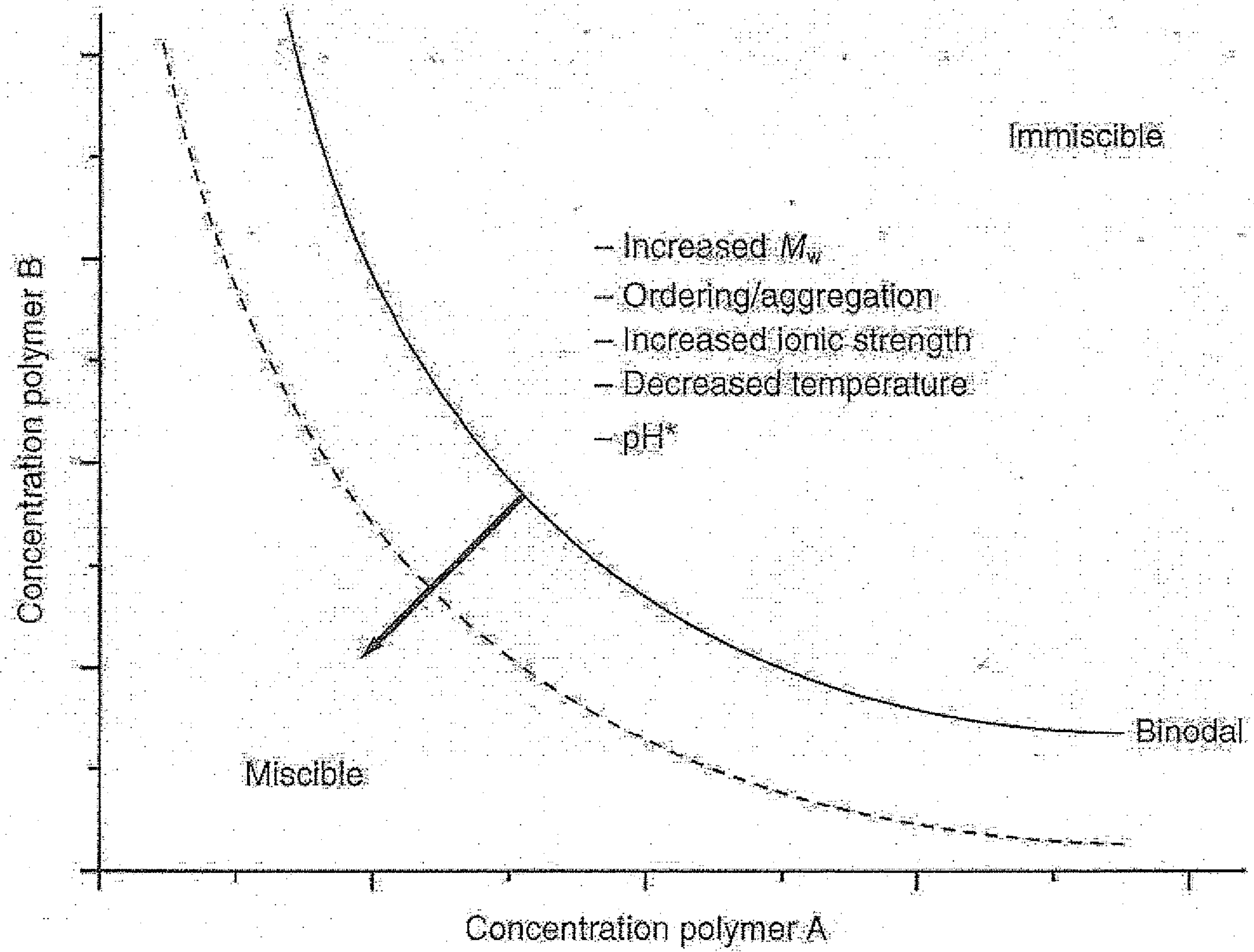
Example: Aqueous mixture of gelatin and maltodextrin



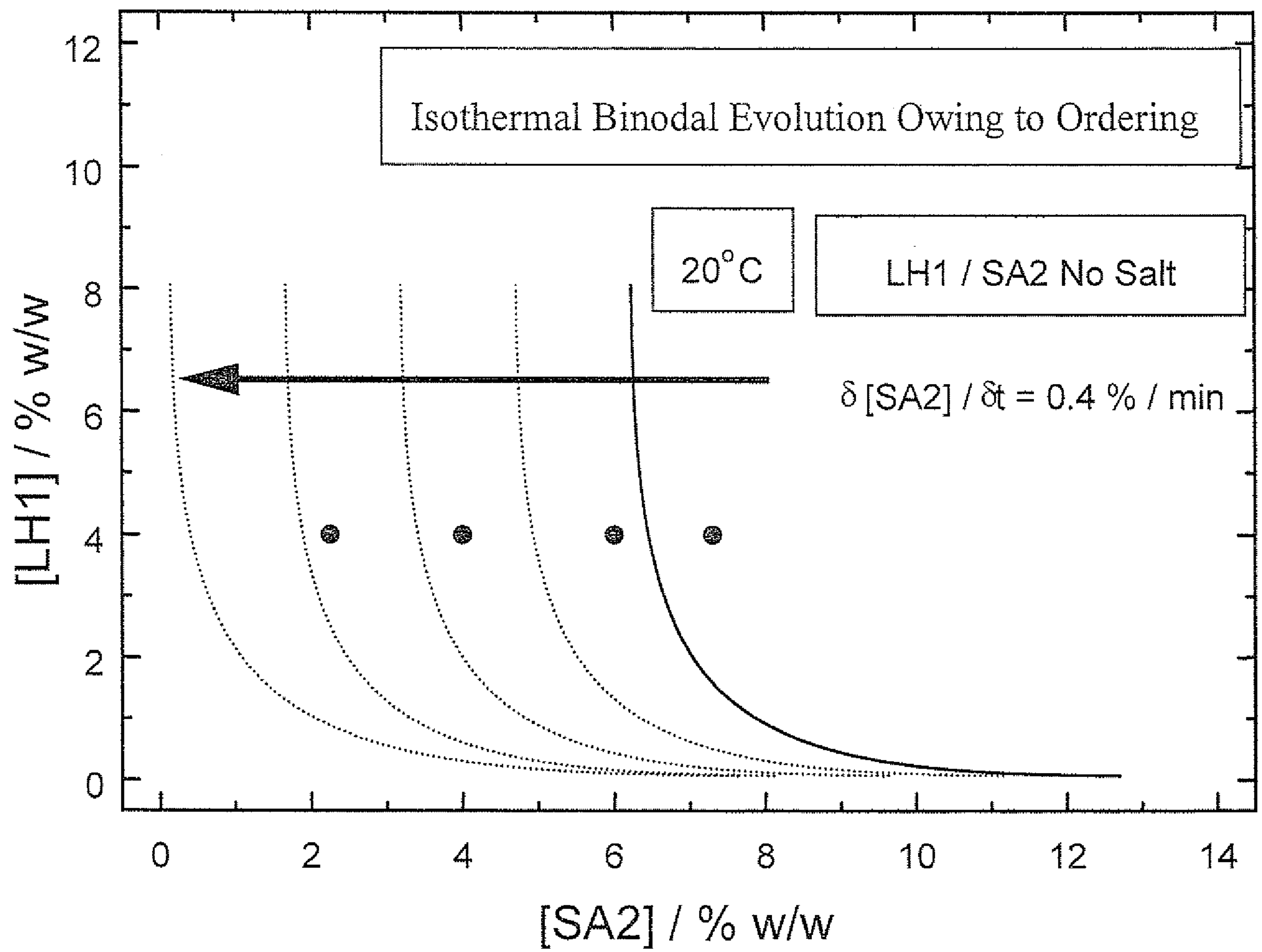
For charged polymers (polyelectrolytes) salt (type and concentration) as well as pH are important parameters.

Bottom phase: Maltodextrin

Influence of varying polymer characteristics



Phase separation driven by molecular ordering of one of the biopolymers.



- Schematic phase diagram showing the binodal as a function of ordering at 20 °C

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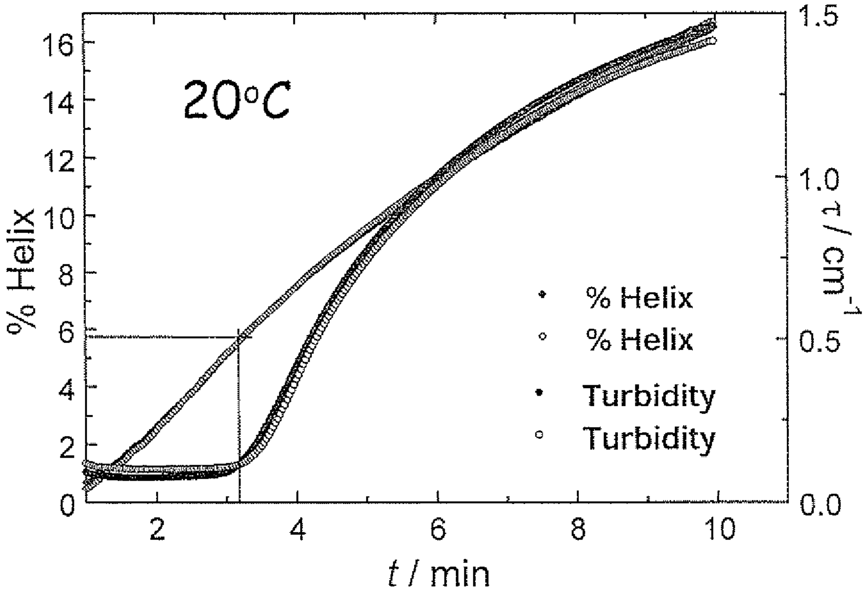
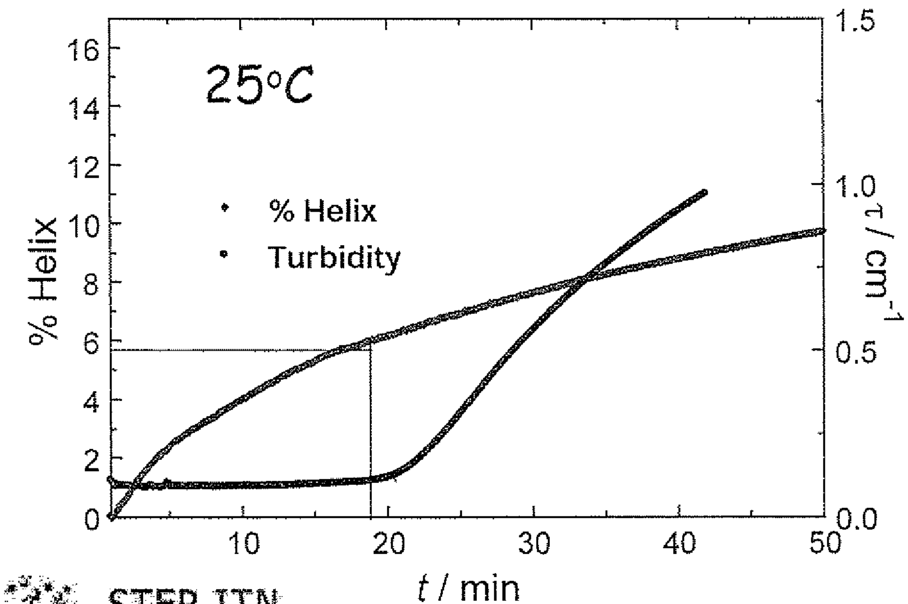
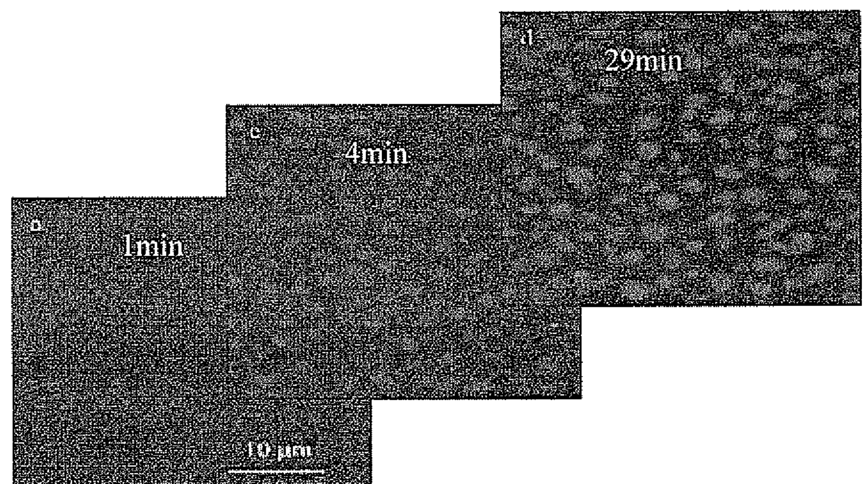
Process effects



Structure induced phase separation.

- Measure of gelatin helices required to induce phase separation in a 4% LH1e:4% SA2 mixture , in water, when quenched to 20°C (top) and 25°C (bottom).
- Morphology when quenched to 20°C.





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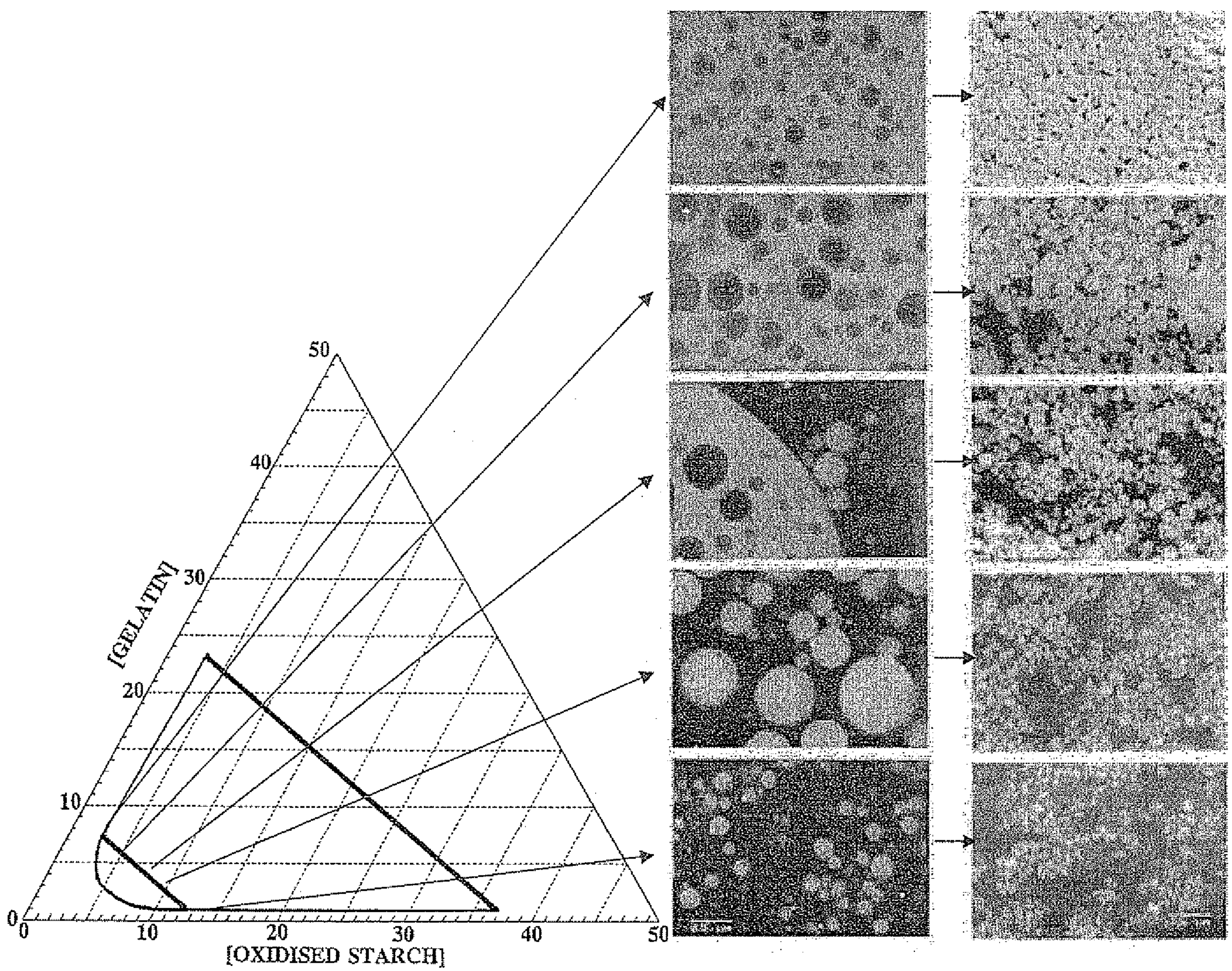
Process effects on mixed biopolymer systems.

Effect of shear during cooling / gelation of the gelatin



Gelling biopolymer forms the dispersed phase.

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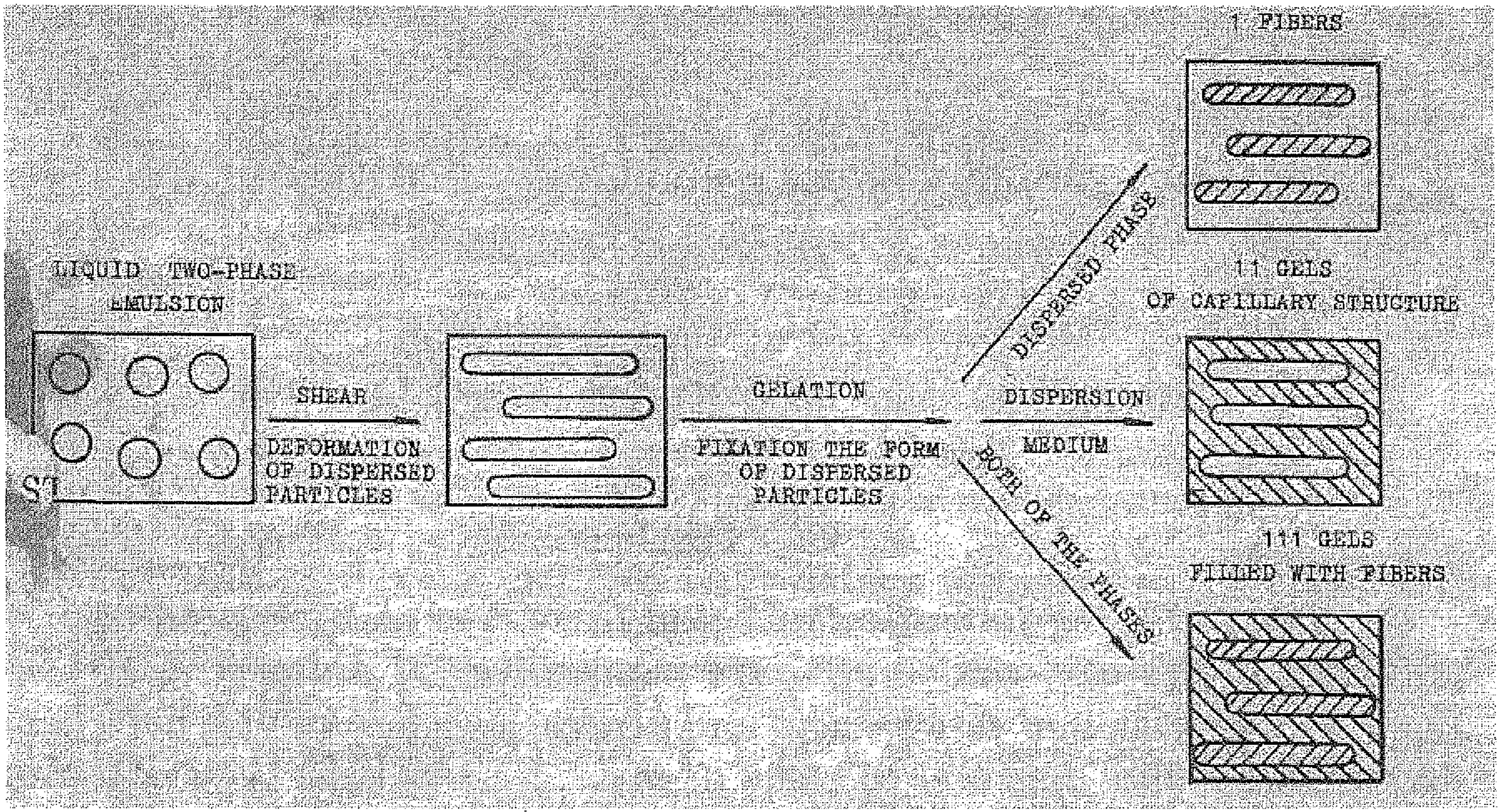
Structures based on aqueous-based two-phase systems

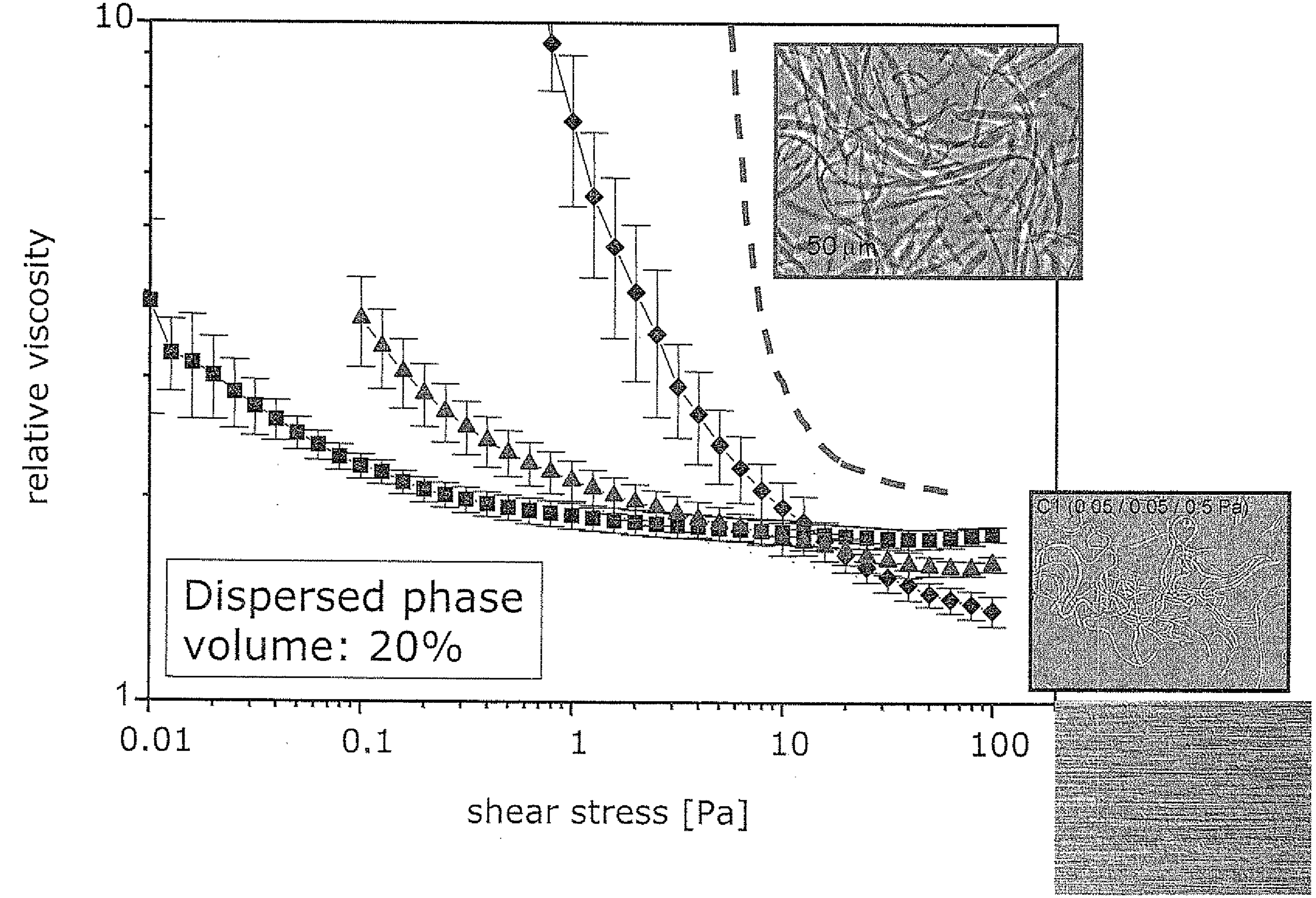
Scheme developed by Tolstoguzov*



*V Tolstoguzov *Journal of Texture Studies* 11, 3 (1980) 199-215

Gel particle suspensions

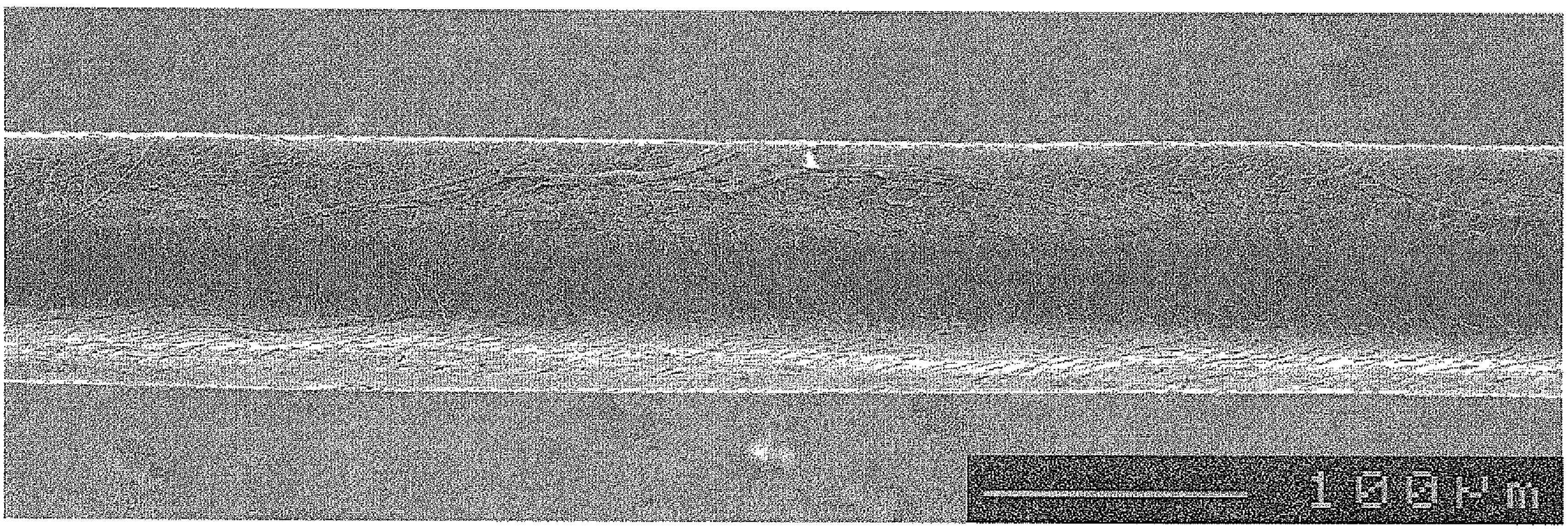
Modification of (shear) rheology: Effect of fibre alignment



Gel particle suspensions

Deposition: Non-food example

κ-carragenan fibres deposited on a hair. Spherical particles of the same composition wash off during rinse.



SEM micrograph by M Kirkland

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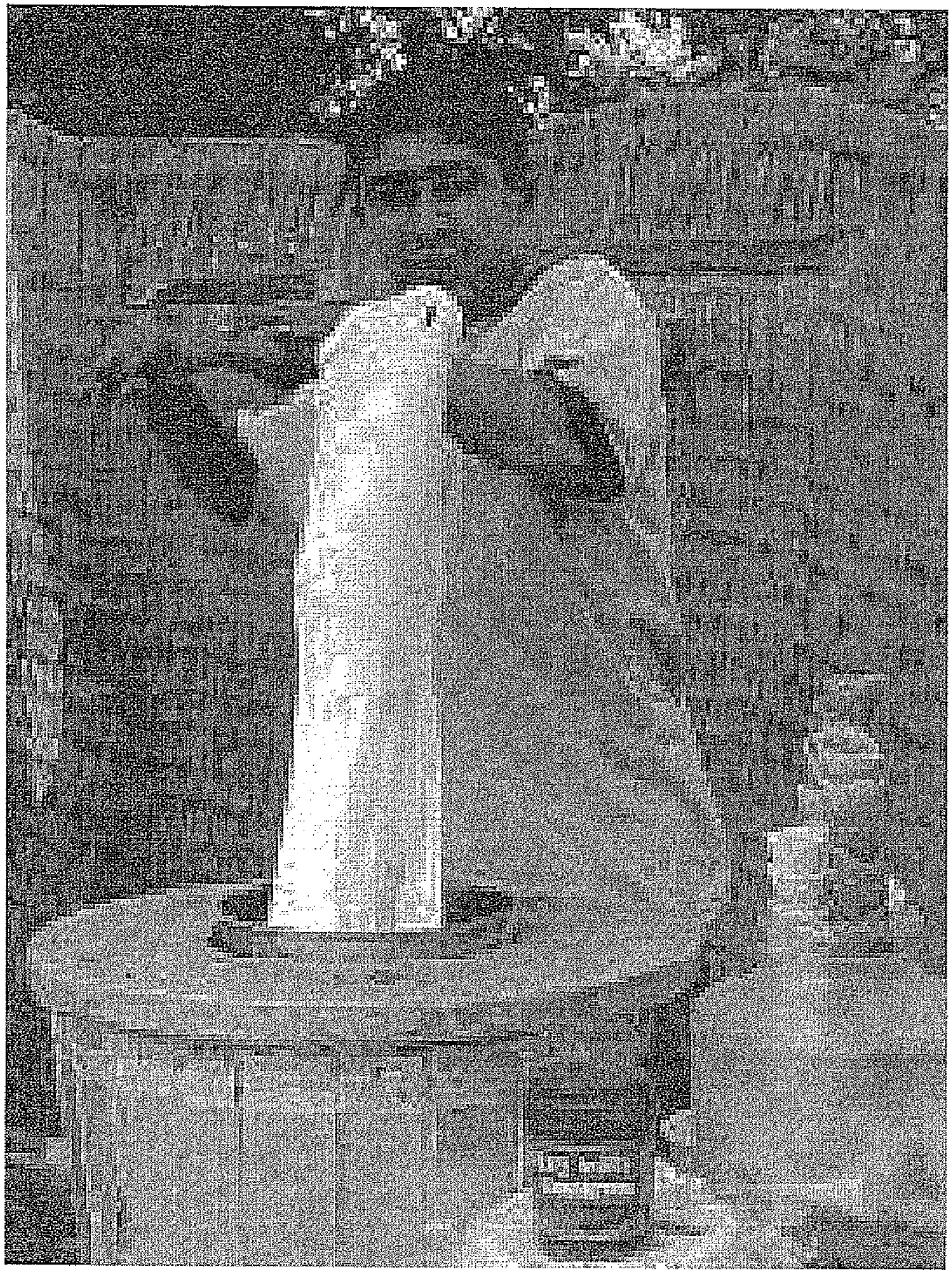

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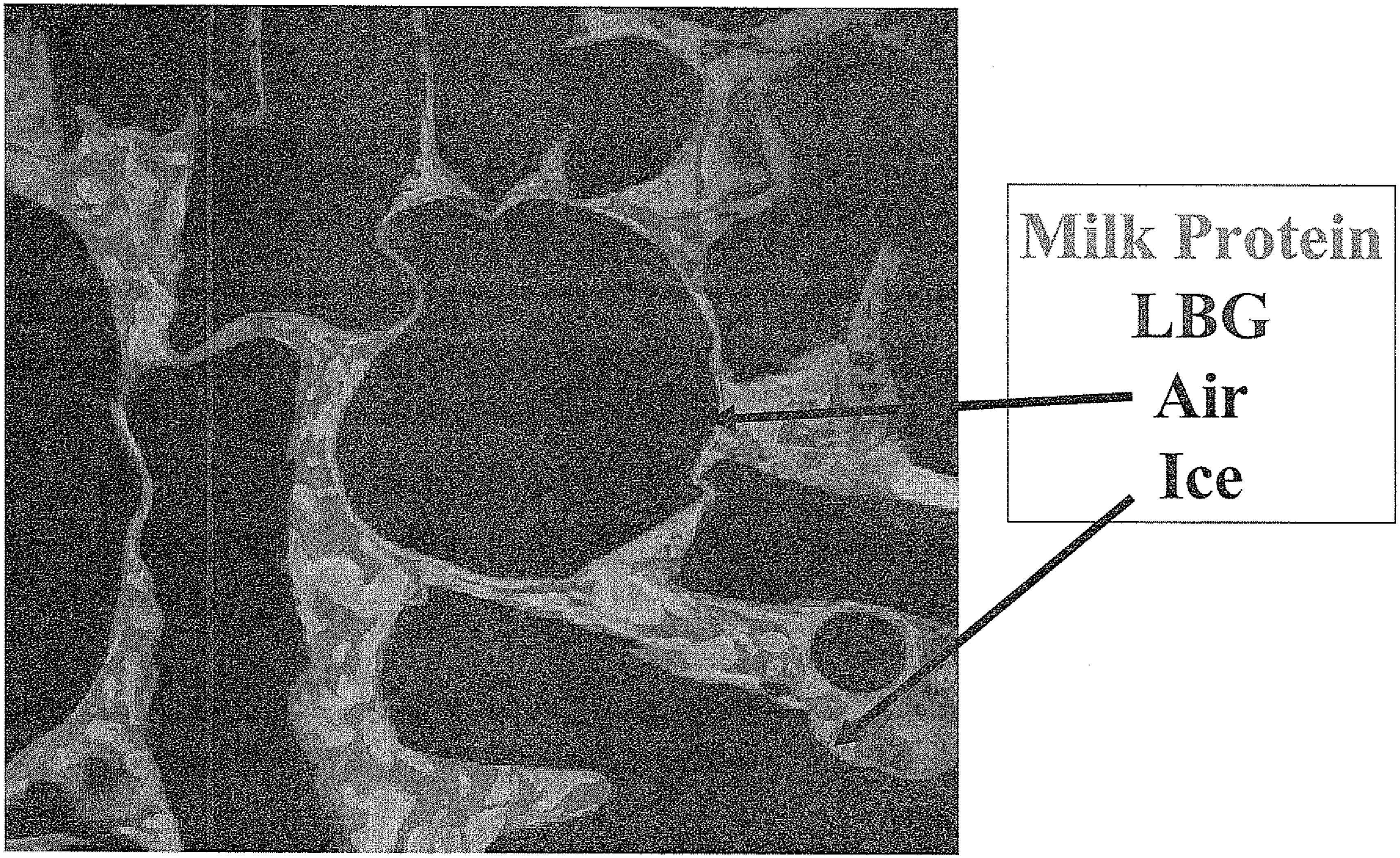
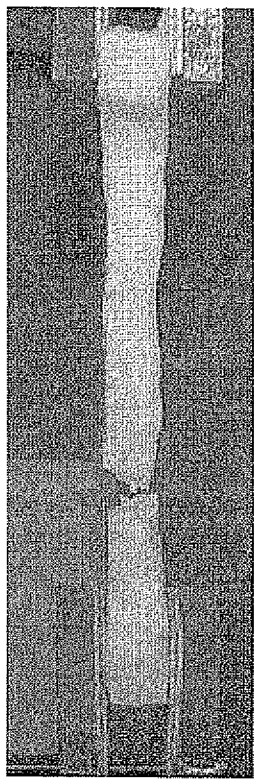
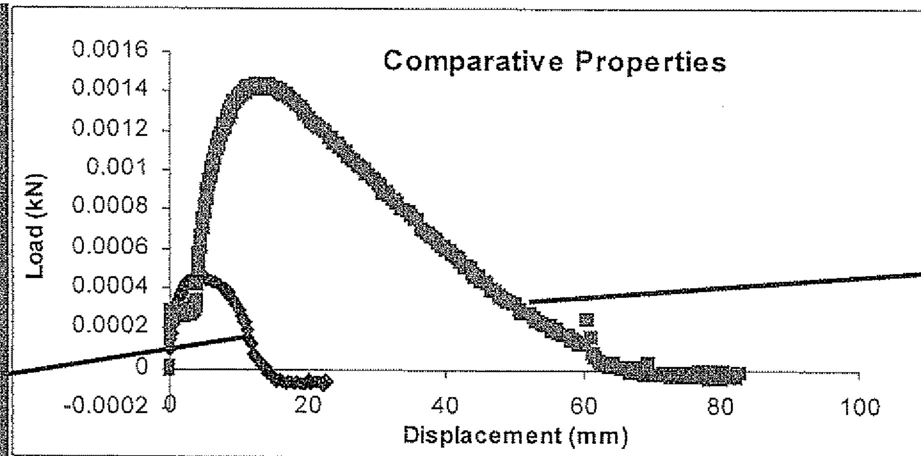
Ice Cream



Maras Ice Cream

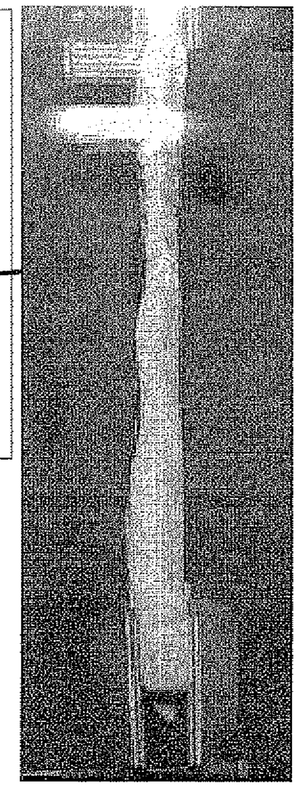


Short texture
ie. snaps



Conventional
Formulation

Maras
Formulation



Extensible texture
ie. stretches

GB 9930531
US 20010031304

STEP ITN

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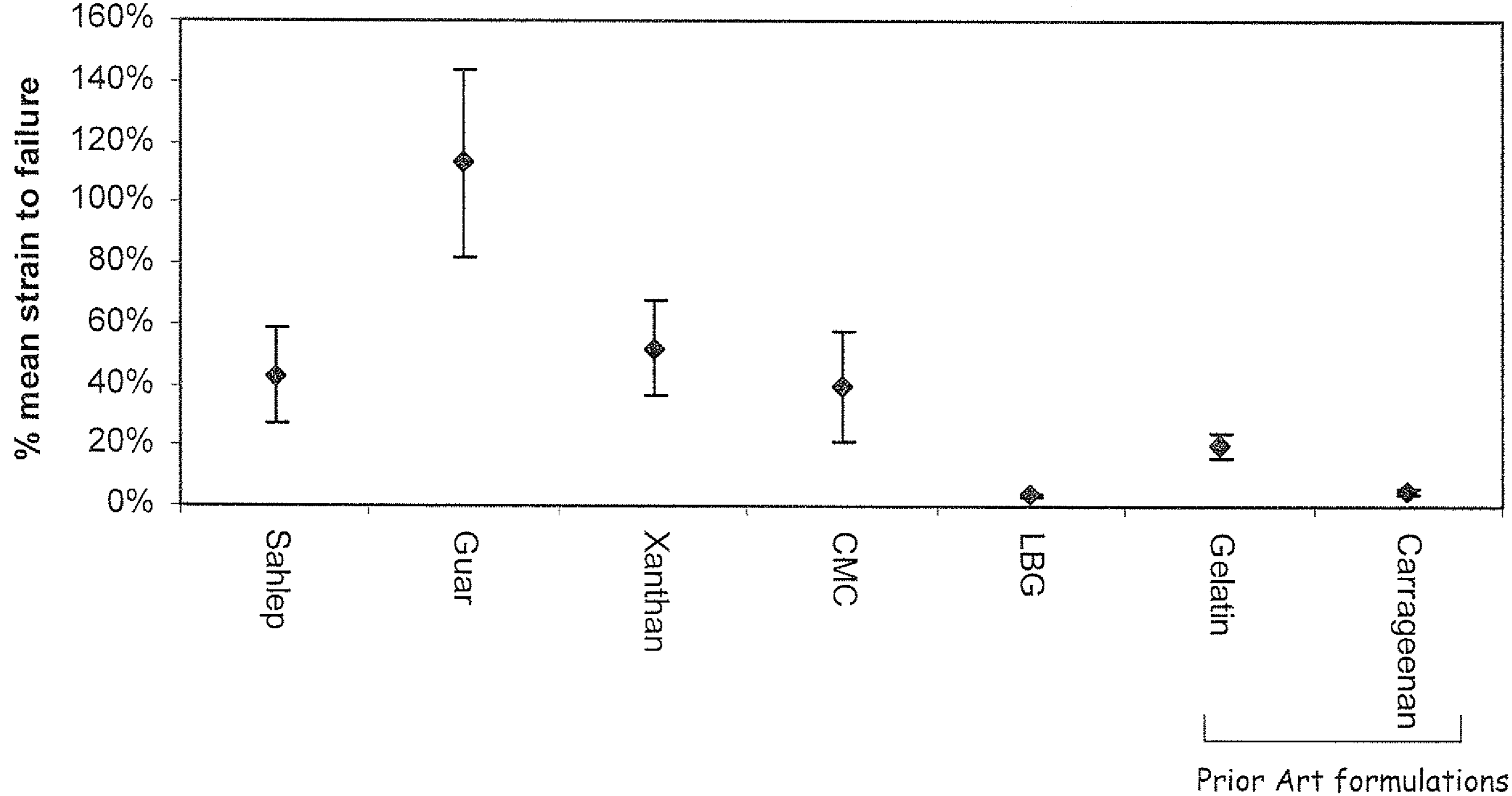
Hydrocolloid functionality in Maras Ice Cream

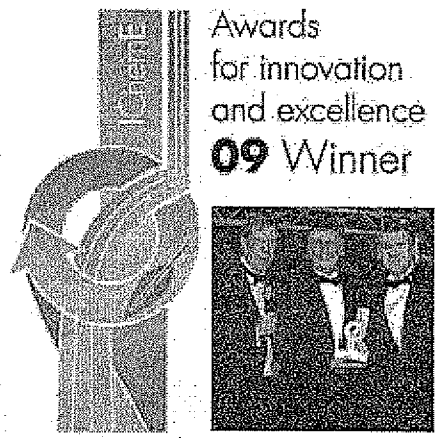


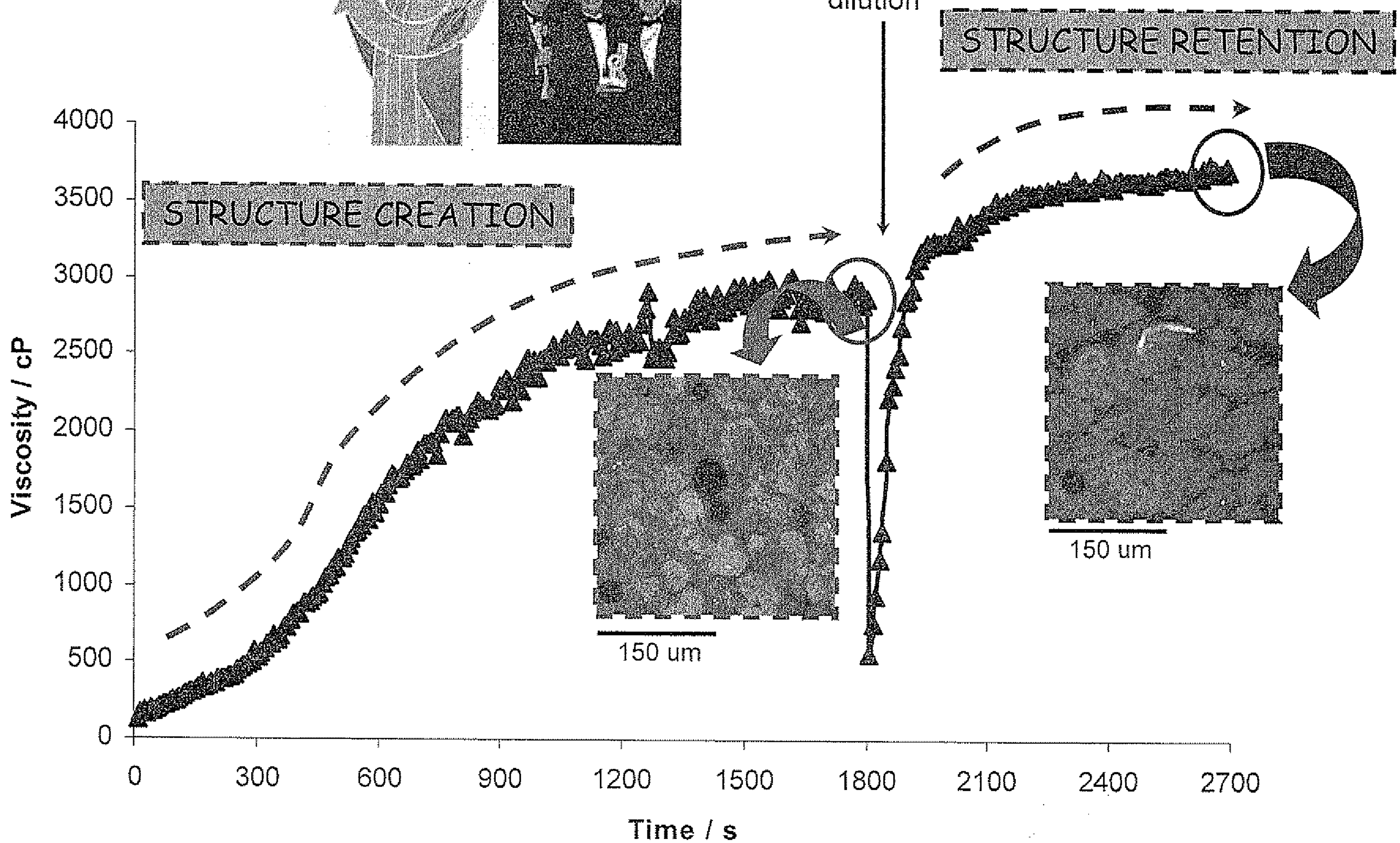
All products here compared at 30% Overrun

Conclusion

- The fine structure of hydrocolloids plays a role in their properties (viscosity and gelation)
- Influence of process can alter the functionality (single and mixed systems)
- Hydrocolloid:Hydrocolloid interactions determine the gross properties of composites

STEP ITN





Acknowledge ALL past and present colleagues for support and stimulation